Finding Solutions for Materials Science

Synchrotron Diffraction and X-ray Absorption Spectroscopy

Joel Reid,
Industrial Scientist,
Canadian Light Source

Wednesday,
May 1, 2019

Outline

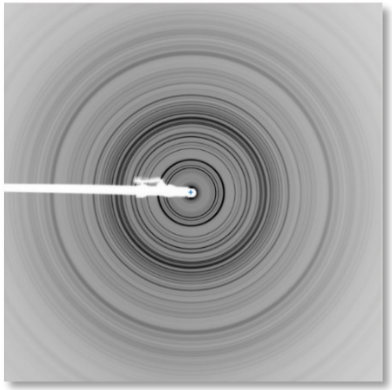
1. Some examples of X-ray diffraction (XRD) techniques available for materials research at the Canadian Light Source, including:
   - Powder X-ray Diffraction (PXRD),
   - Single Crystal X-ray Diffraction (SC-XRD),
   - Laue microdiffraction with the VESPERS beamline,
   - Thin film analysis with the IBM endstation.

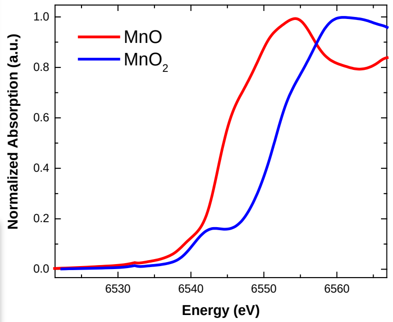
2. Some examples of X-ray absorption spectroscopy (XAS) and spectromicroscopy (SM) for materials research.

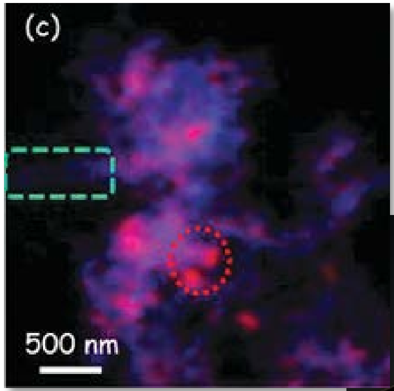
Overview of Synchrotron Techniques

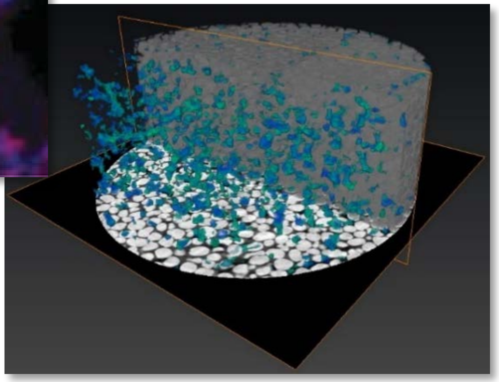
Synchrotron techniques can be divided into four major areas:

1. **Diffraction:**
   - Crystal structure and microstructure determination.
   - Quantitative phase analysis.
2. **Spectroscopy (X-ray and IR):**
   - Oxidation states.
   - Chemical species.
3. **Spectromicroscopy (X-ray and IR):**
   - Combination of imaging and spectroscopy.
   - Mapping of species and chemical states.
4. **Imaging:**
   - Synchrotron version of medical x-rays/CT.
   - High contrast and large field of view.









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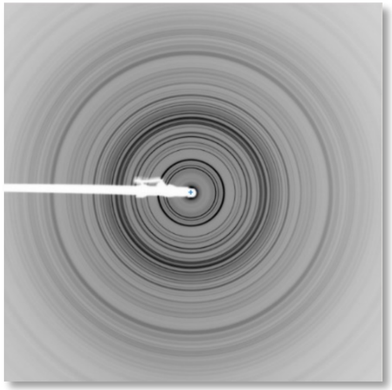
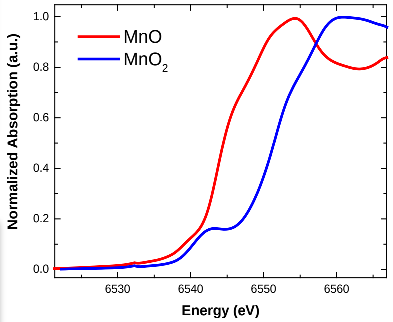
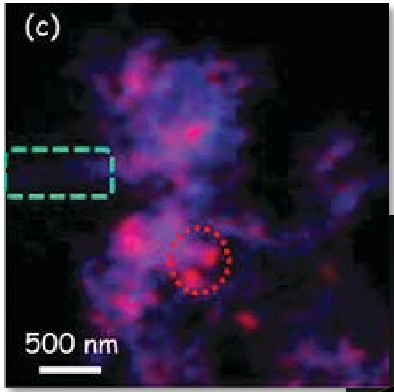
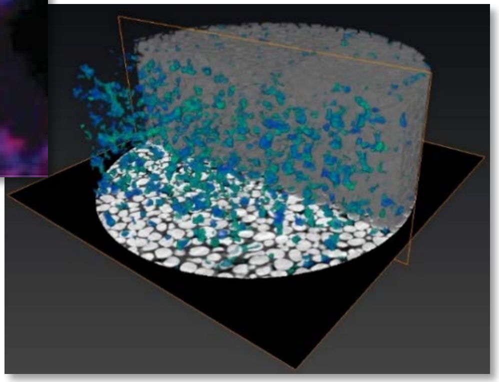


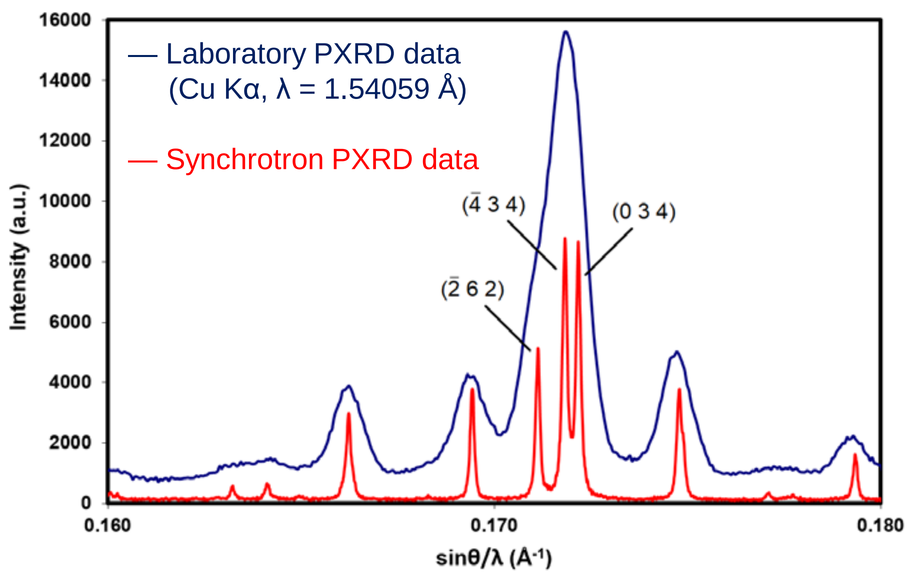






Why Synchrotron Powder X-ray Diffraction (PXRD)?

- Synchrotron sources provide a number of distinct advantages for powder diffraction:
  - **High resolution** (thinner peaks than a laboratory diffractometer).
  - High intensity (short data collection times, improves application of diffraction to time-resolved studies and small sample volumes).
  - Excellent signal-to-noise and intensity estimates from large 2D detectors.
  - Tunable energy over a wide range, facilitating anomalous dispersion & pair distribution function (PDF) techniques:
    - CMCF: E = 4 to 18 keV (λ = 3.1 to 0.69 Å).
    - Brockhouse: E = 7 to 90 keV (λ = 1.8 to 0.14 Å)



Canadian Light Source Centre canadien de rayonnement synchrotron

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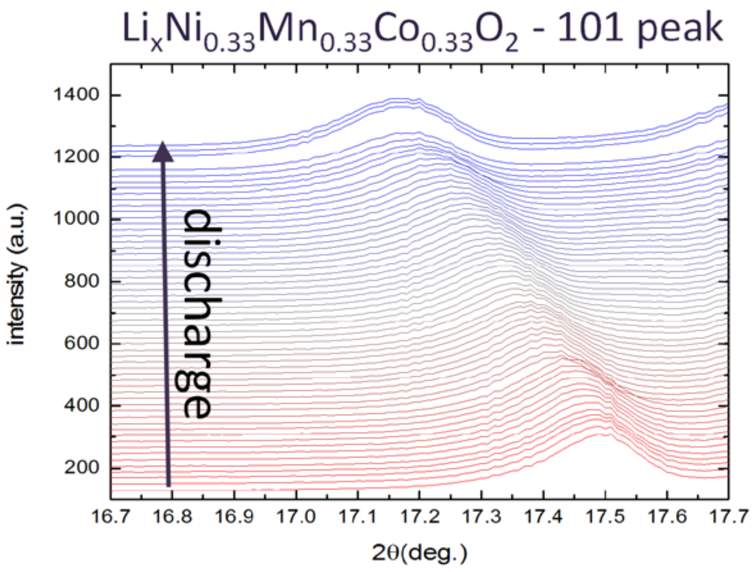

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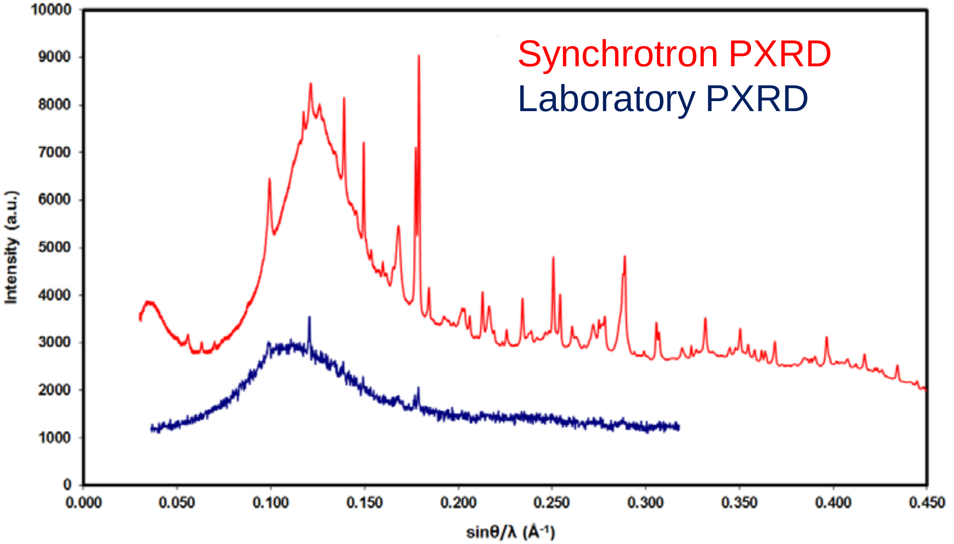

Reid, J., *et al.*
SPE Journal 22 (2017) 875-880.

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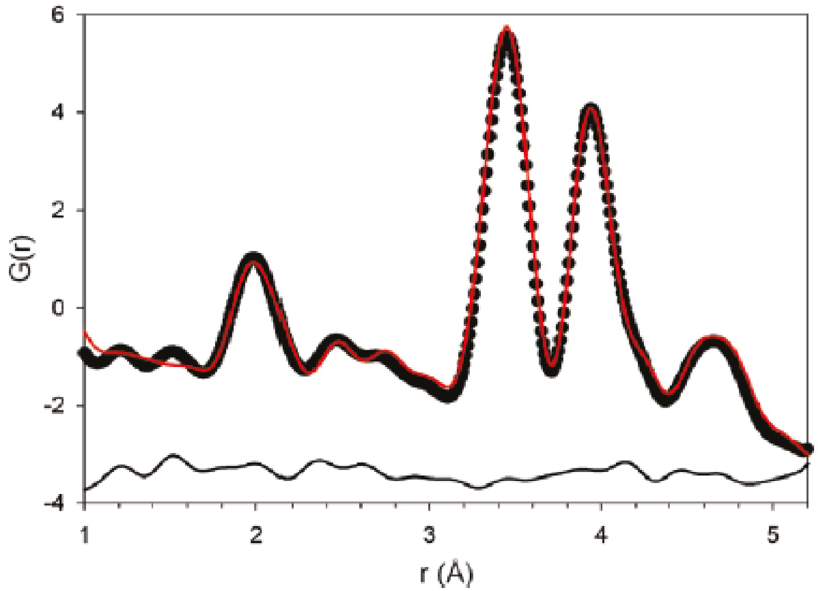
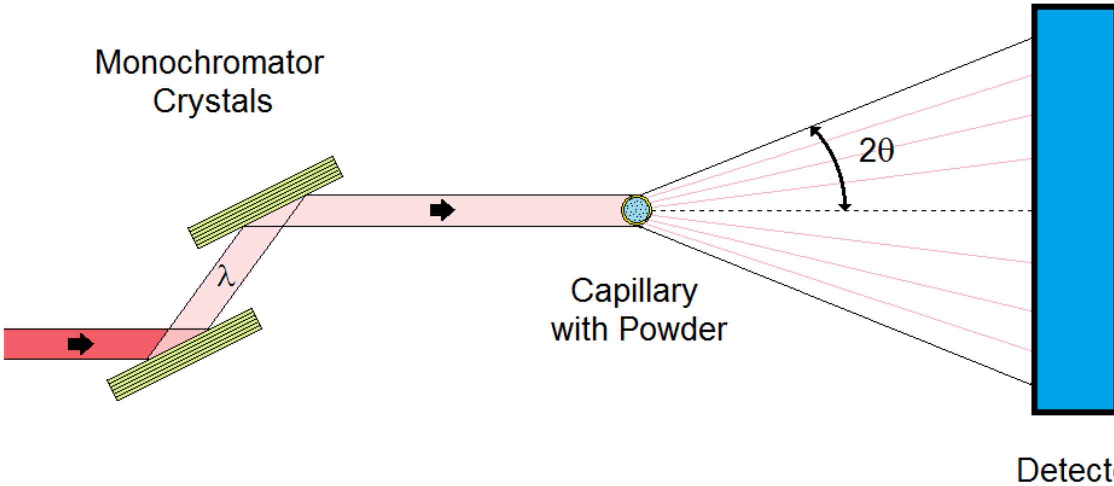


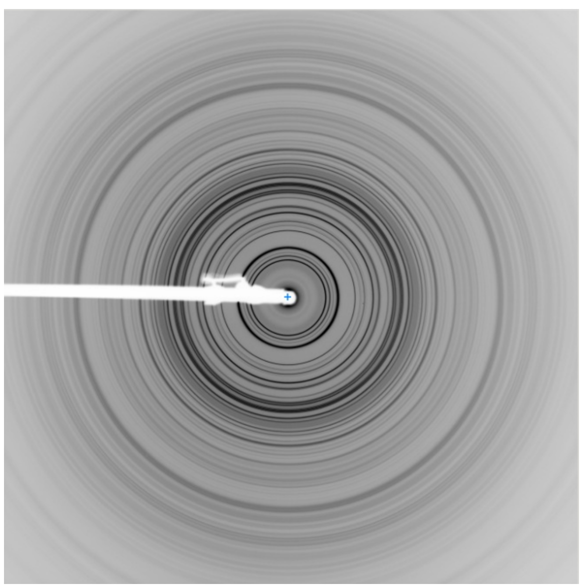
Dachraoui, W., *et al.* *Chem. Mater.* 23 (2011) 2398-2406.

Powder X-ray Diffraction (PXRD) on CMCF-BM

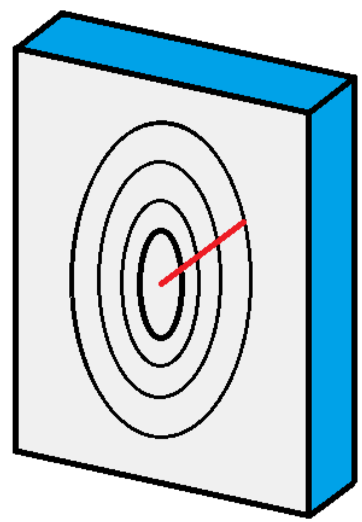


Debye-Scherrer
Transmission
Geometry

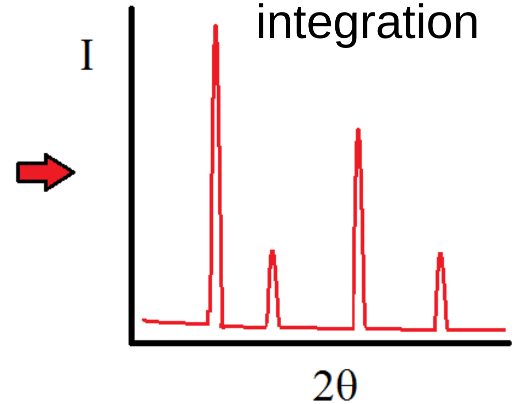
E = 18 keV
λ = 0.68880 Å



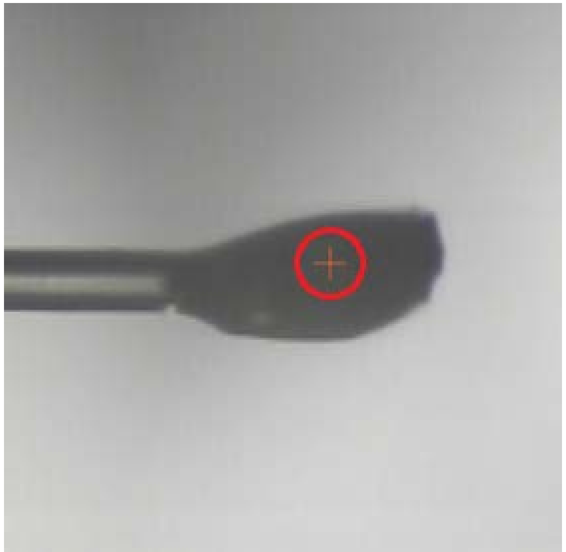
2D powder
ring pattern
on detector



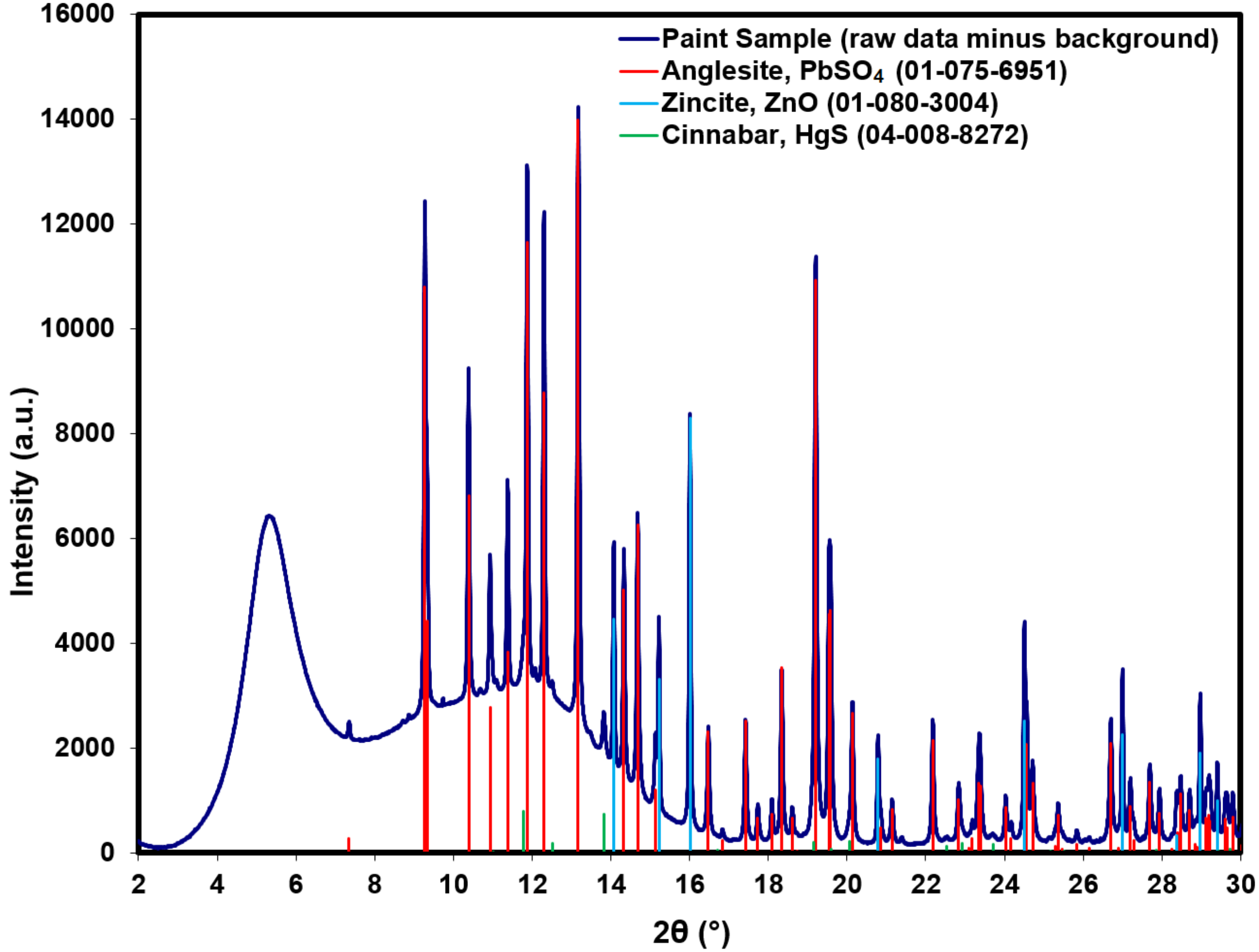
1D powder
pattern after
integration



PXRD Applications: Very Small Samples

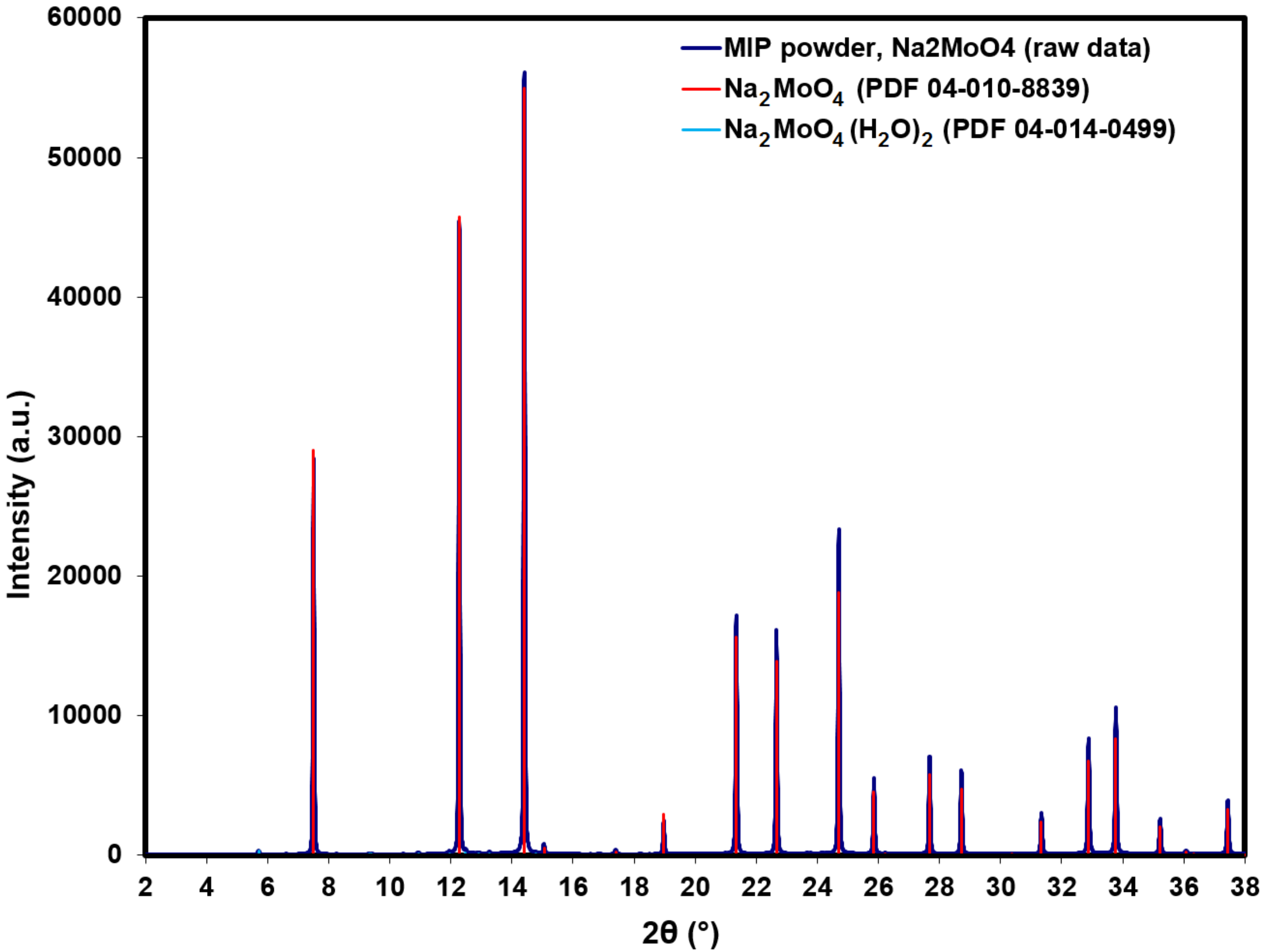


100 µm spot size

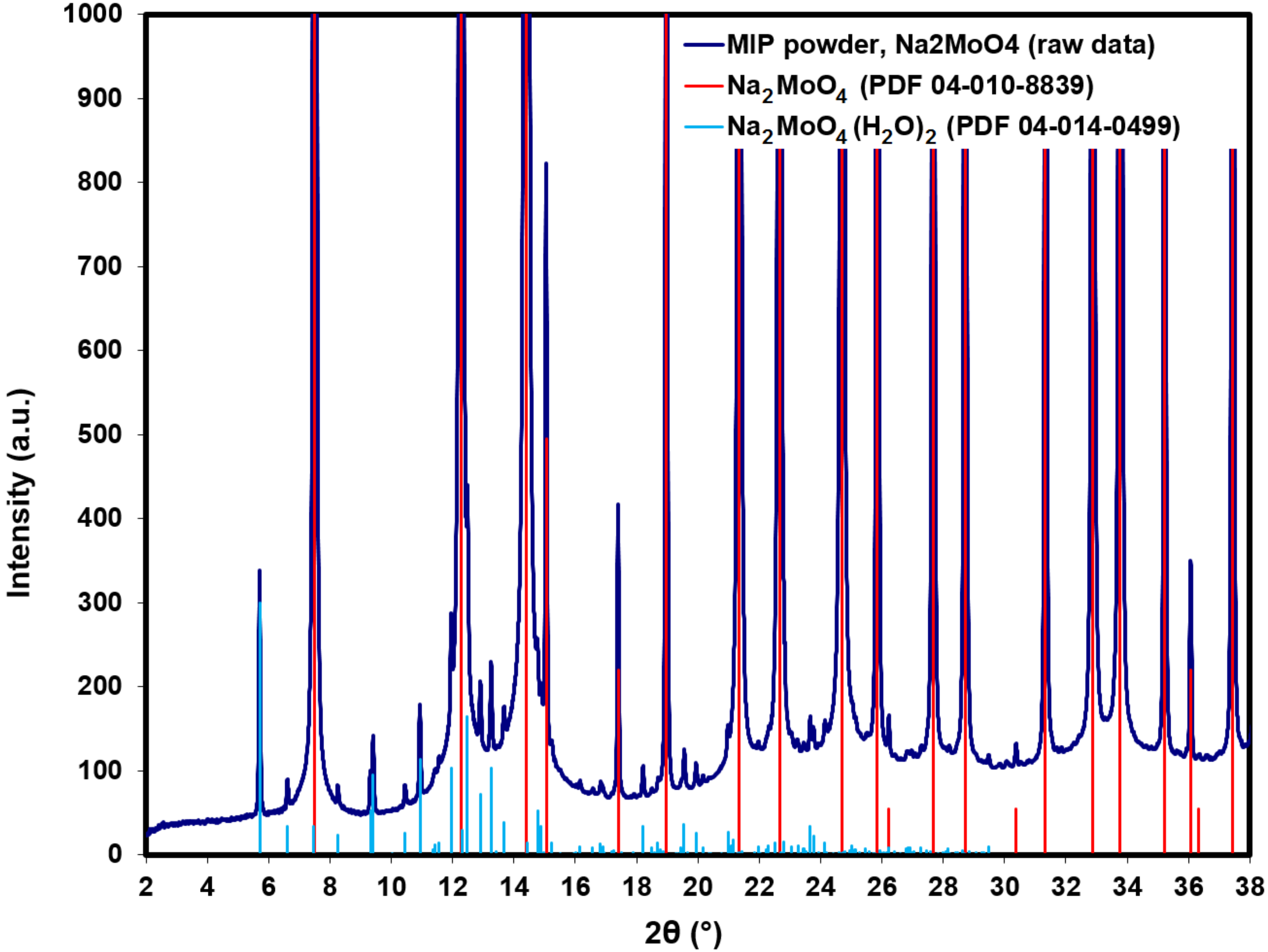


Data courtesy of Marie-Claude Corbeil (Canadian Conservation Institute).

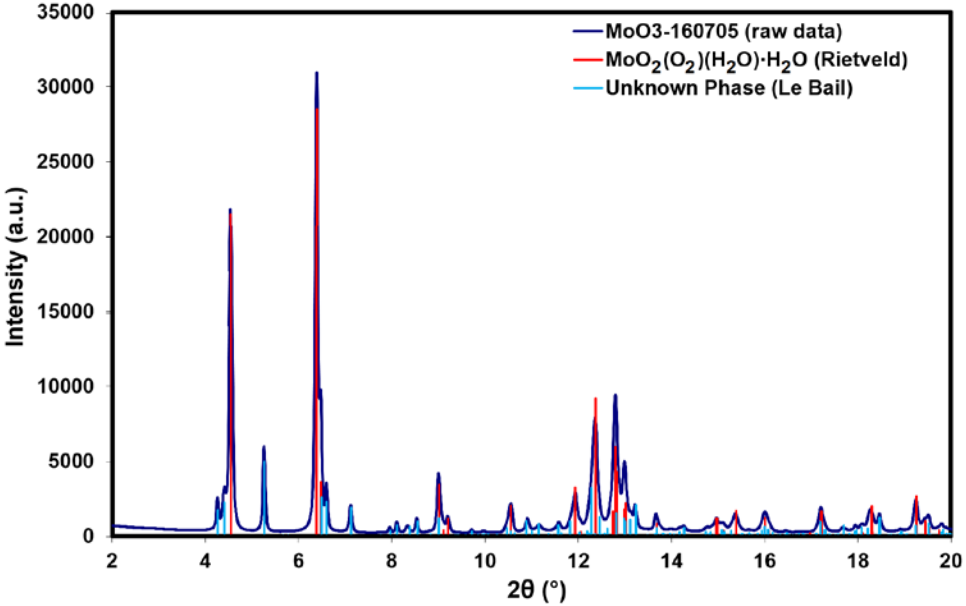
PXRD Applications: Trace Phase Analysis

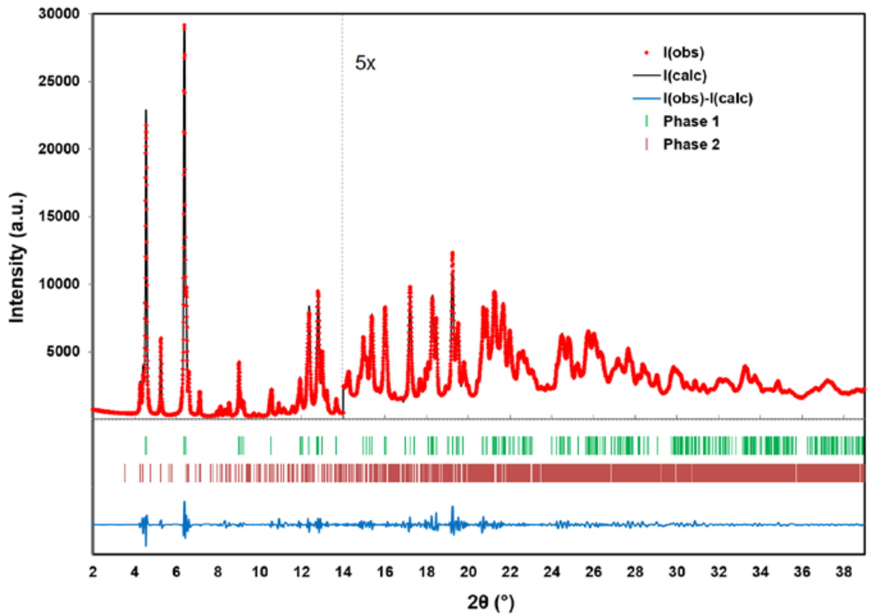


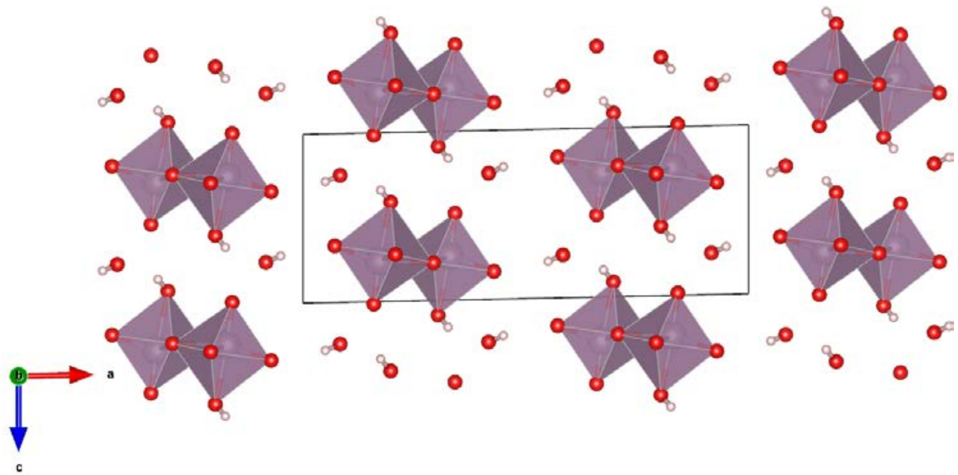
PXRD Applications: Trace Phase Analysis (cont.)



PXRD Applications: Crystal Structure Solution







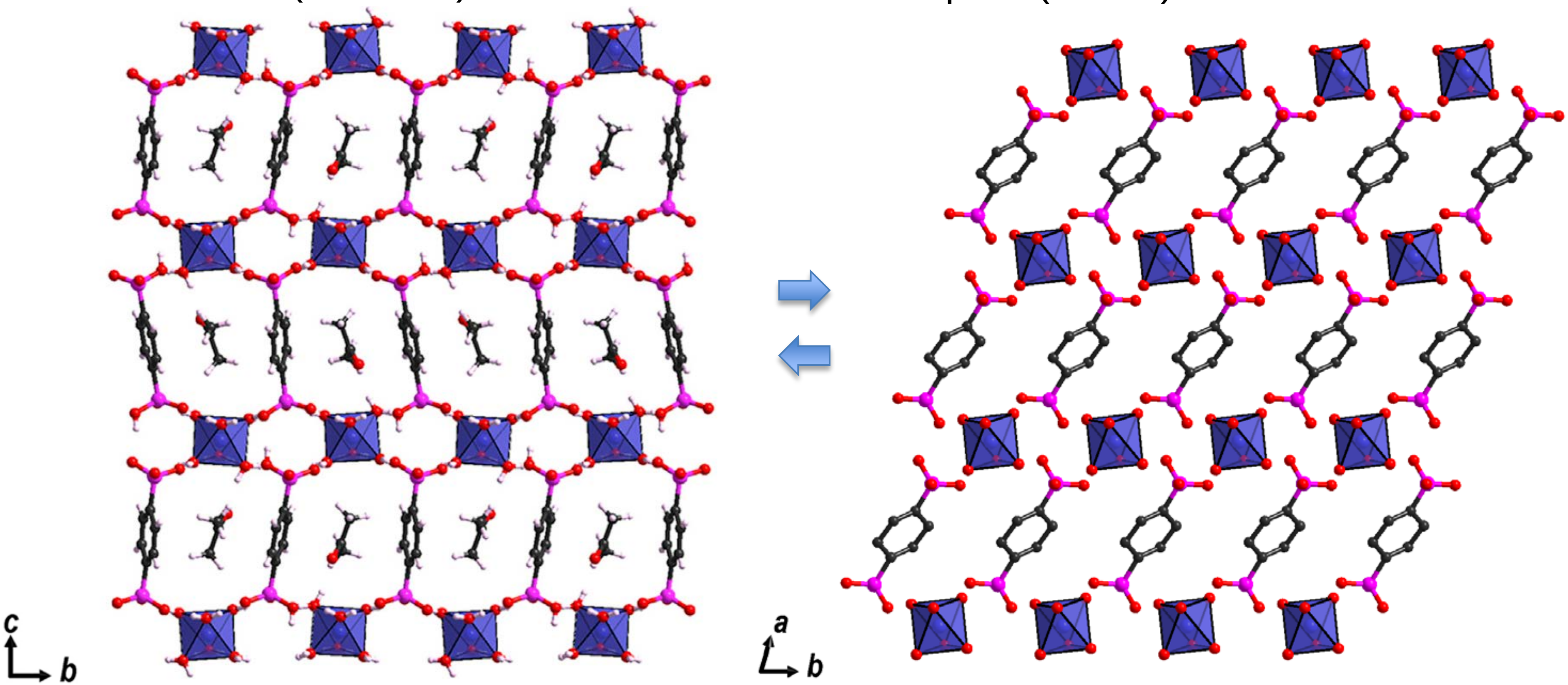
$MoO_2(O_2)(H_2O)\cdot H_2O$

Reid, J.W., Kaduk, J.A. & Matei, L.
Powder Diffraction 34 (2019) 44-49.

PXRD Applications: Structure Solution (HOFs)

Acetone loaded (SC-XRD)

Closed pore (PXRD)



$[Cr(H_2O)_6]$ $[O_3P\text{-}C_6H_4\text{-}PO_3H] \cdot CH_3COCH_3$

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Taylor, J.M., *et al*.
Chem 4 (2018) 868-878.

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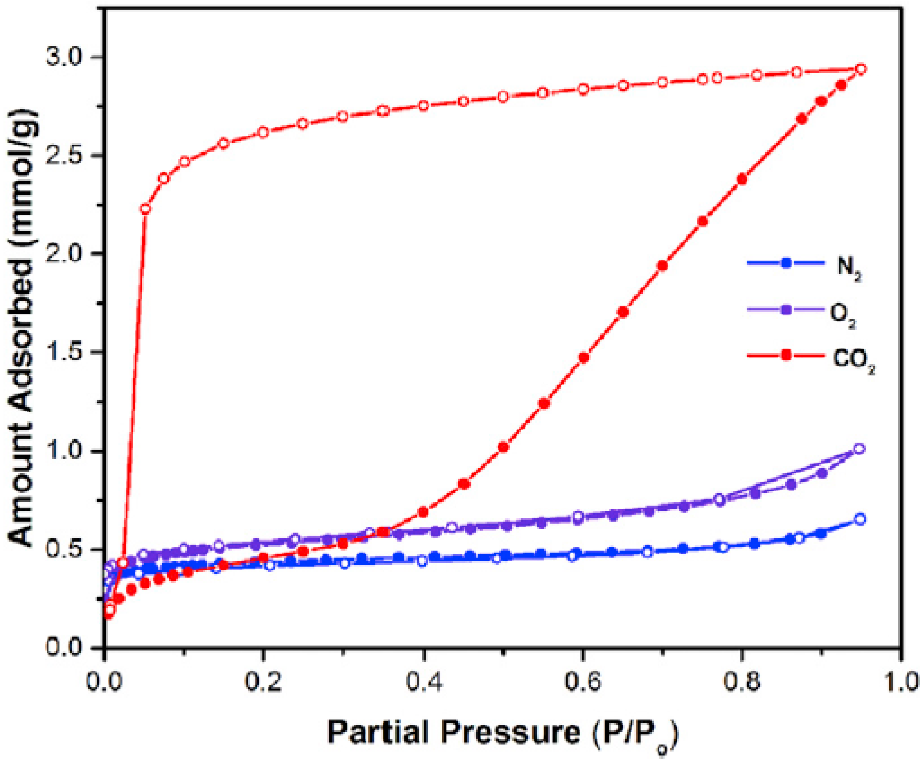
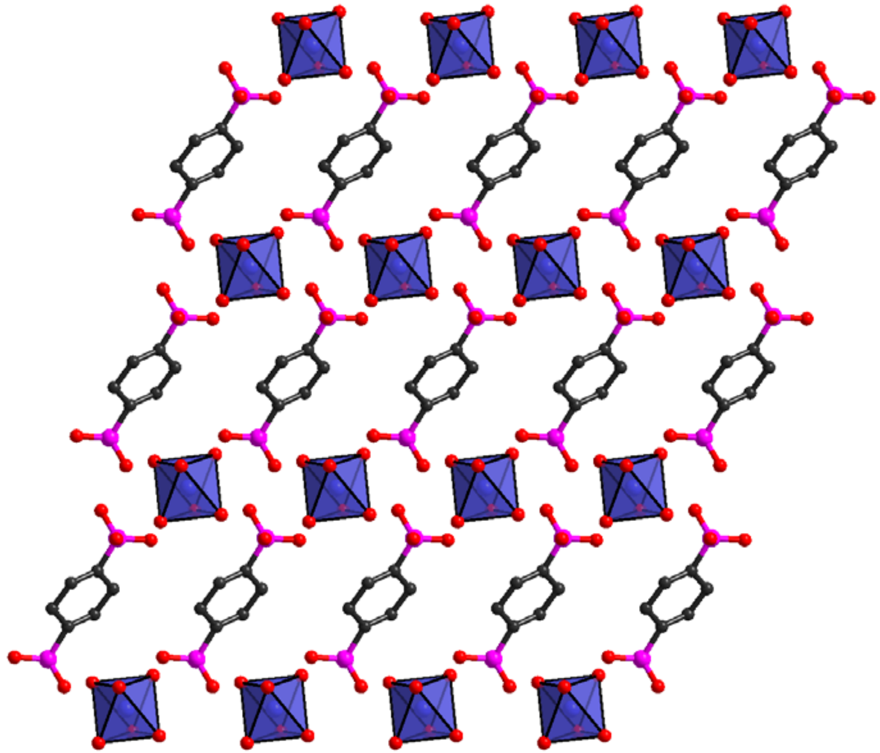


Closed pore (PXRD)



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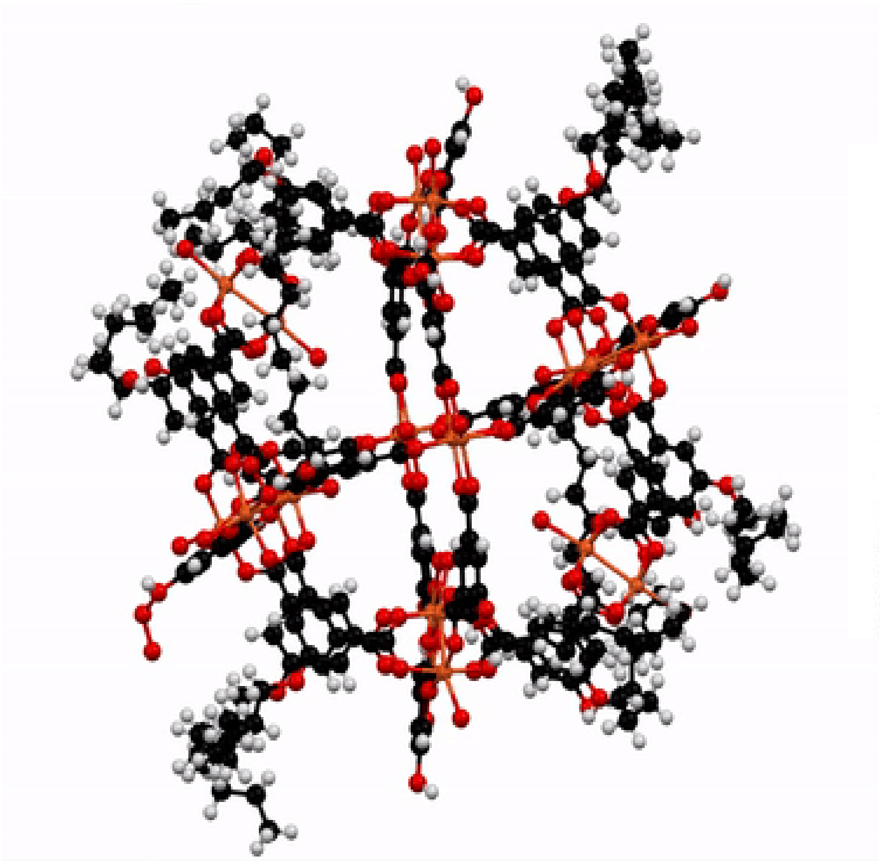
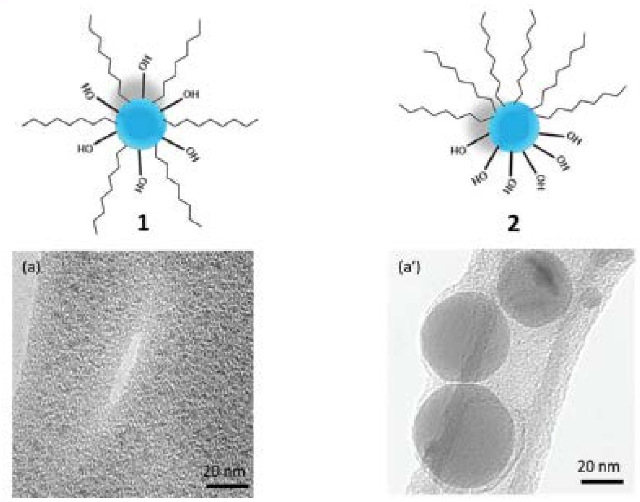
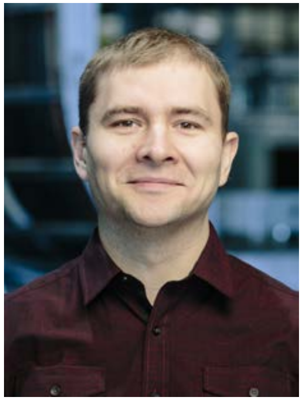
Small Molecule Single Crystal XRD

- The behavior of metal-organic polyhedra (MOPs) in solution depends on the distribution of surface ligands, allowing the surface chemistry to be tailored to specific applications.







Denis Spasyuk

Lal, G., Lee, S.J., Spasyuk, D.M. & Shimizu, G.K.H. *Chem. Commun.* 54 (2018) 1722-1725.

Powder and Single Crystal XRD Mail-In Programs

- We have mail-in programs! Rapid access PXRD and single crystal XRD forms can be accessed at:
  - **https://www.lightsource.ca/industry**

- **Easy:** Simple form, no contract.

- **Affordable:** Data starting at $65 per data set.

- **Quick turnaround:** Typically 1 to 2 weeks.

CANADIAN LIGHT SOURCE Inc. POWDER DIFFRACTION ANALYSIS REQUEST FORM

Canadian Light Source Centre canadien de rayonnement synchrotron

Sample Id	Formula	Colour	Composition (wt% or at%) or Major Elements	Requested Analysis/Charges Data Collection $130	Prep and Data Collection $160	Phase ID $550	Additional Work $150
				☐	☐	☐	☐
				☐	☐	☐	☐
				☐	☐	☐	☐
				☐	☐	☐	☐
				☐	☐	☐	☐
				☐	☐	☐	☐
				☐	☐	☐	☐
				Academic Discount (50%) ☐		Total:	

	Client Information:	Billing Information:	CLSI Technical Contact:	CLSI Industrial Science Contact:
Company Name:			Canadian Light Source Inc.	
Contact Name:			Joel Reid	Erika Bergen
Phone:			306-657-3854	306-657-3867
Email:			joel.reid@lightsource.ca	erika.bergen@lightsource.ca
Address:			44 Innovation Blvd, Saskatoon, SK S7N 2V3, Canada	
PO#:				

Description of work:

1) **Data Collection**: This package includes data collection and calibration for capillary samples prepared by the client. Data can be formatted in numerous common powder diffraction data formats based on your software requirements.
2) **Prep and Data Collection**: This package includes sample preparation (capillary packing), data collection and calibration. Data can be formatted in numerous common powder diffraction data formats based on your software requirements.
3) **Phase ID**: This package includes sample preparation (capillary packing), data collection, calibration and database search/match for phase identification. Phase identification results are presented in a formal report with a semi-quantitative estimate of the relative crystalline phase composition.
4) **Additional Work**: Additional work charges may apply for complex structures (client will be contacted if additional work is required).

Please inquire about additional PXRD services, offered by customized quotes to meet your needs, including *ab initio* unit cell indexing, Rietveld structure refinement, relative crystalline quantitative phase analysis (QPA), and total QPA (including amorphous content) using an internal standard.

Researchers are asked to report any publications based on work performed, in whole or in part, at the Canadian Light Source or CLS@APS Programme. The list of the publications reported to the CLS is in important factor in our funding and is taken into account during peer review of research proposals. http://www.lightsource.ca/acknowlegements.html

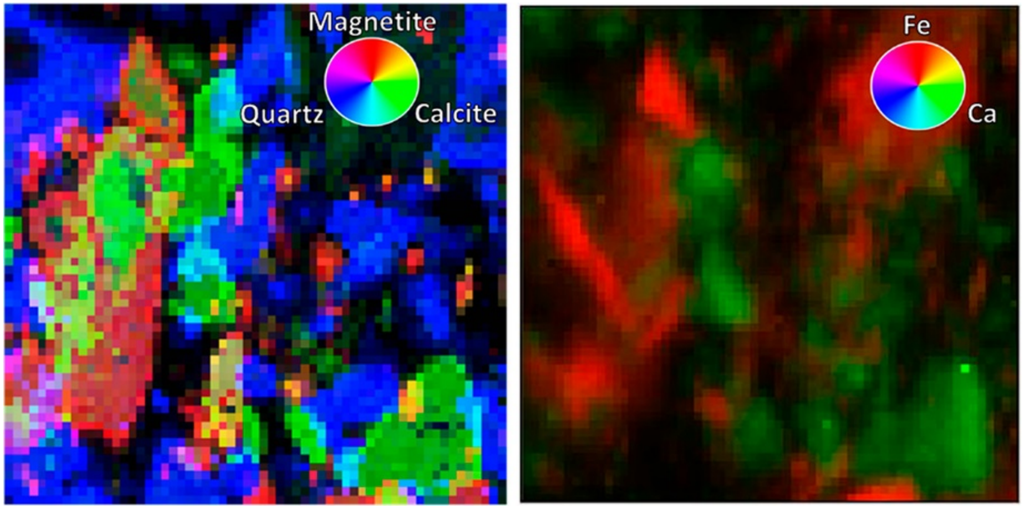
By signing and returning this form, the Client relinquishes the above listed samples to the Canadian Light Source Inc. and authorizes the above listed analysis. Client has read and is in agreement with the Canadian Light Source Standard Terms and Conditions http://www.lightsource.ca/termsandconditions

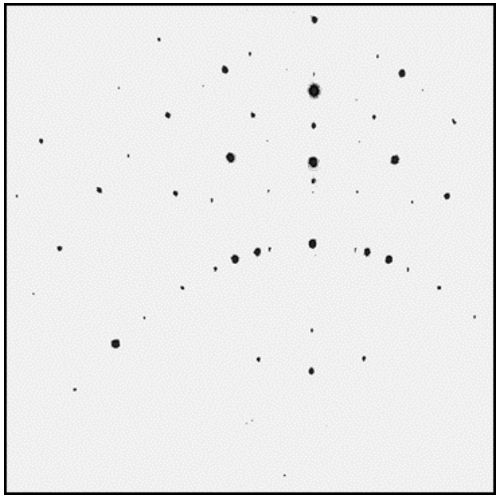
Client Signature:	Date:

For Internal Use Only

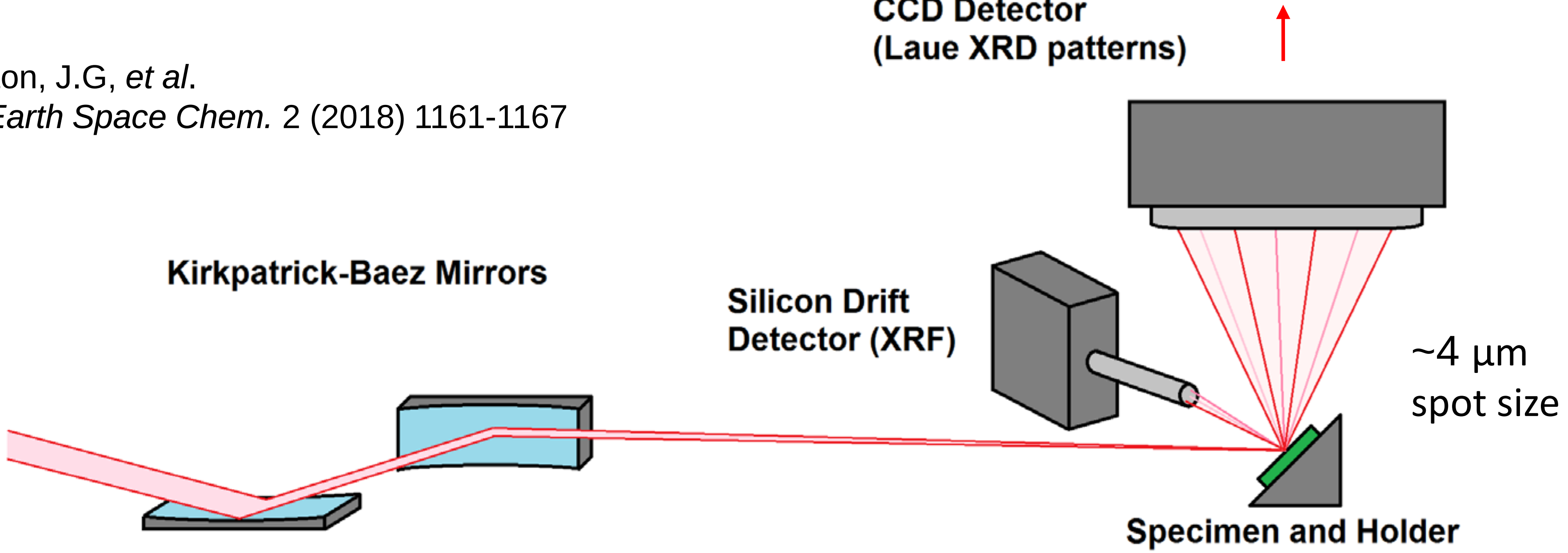
Sample Received (Date):_____________ Initial:_______ Work Completed (Date): _____________ Initial:_______ Contract #_____________ Invoice #_____________ Initial:_______

Microprobe XRD with XRF: The VESPERS Beamline

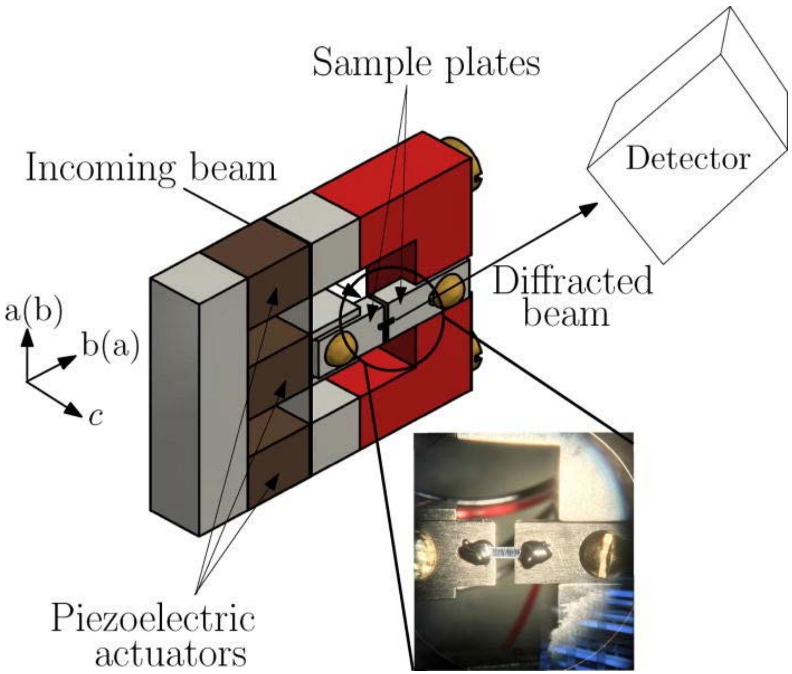




Hamilton, J.G, *et al*.
ACS Earth Space Chem. 2 (2018) 1161-1167



Twinning in $La_{2-x}Sr_xCrO_4$ Under Applied Stress



Imaging twin domains in $La_{2-x}Sr_xCuO_4$
 - Experimental setup.

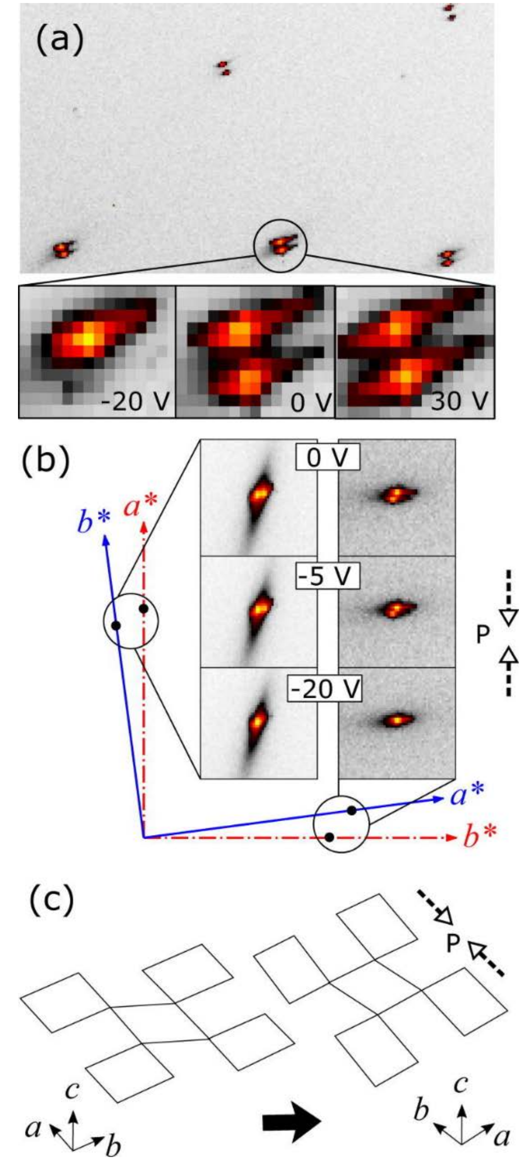
Zheng, X.Y, *et al*.
Appl. Phys. Lett. 113 (2018) 071906.

(**a**) Partial diffraction pattern under no strain, with views at −20 V, 0 V, and +30 V.

(1 V = ~ 1 MPa)

(**b**) The reciprocal space perpendicular to c-axis for the two twin domains. Circles - Bragg peak positions for (200) and (020) peaks.

(**c**) Real-space schematics illustrating the response of CuO_2 planes in LSCO under compressive strain. The buckled rectangles represent CuO_6 octahedra. Note the elongation along the compression direction.



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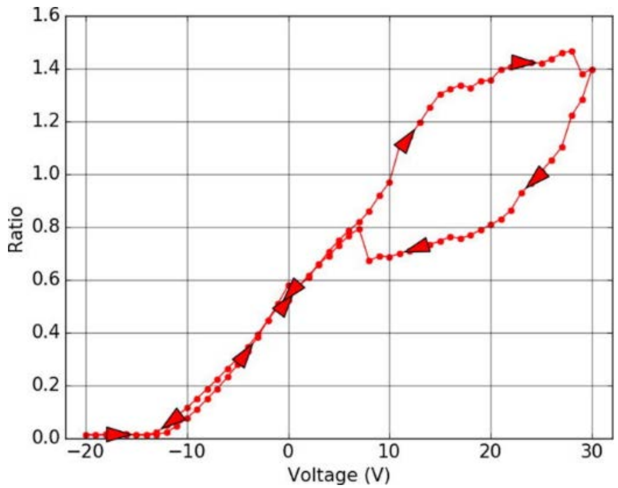

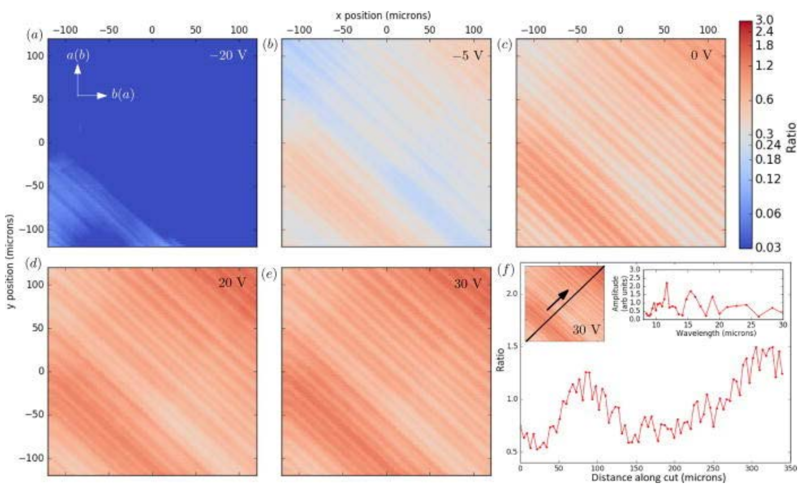

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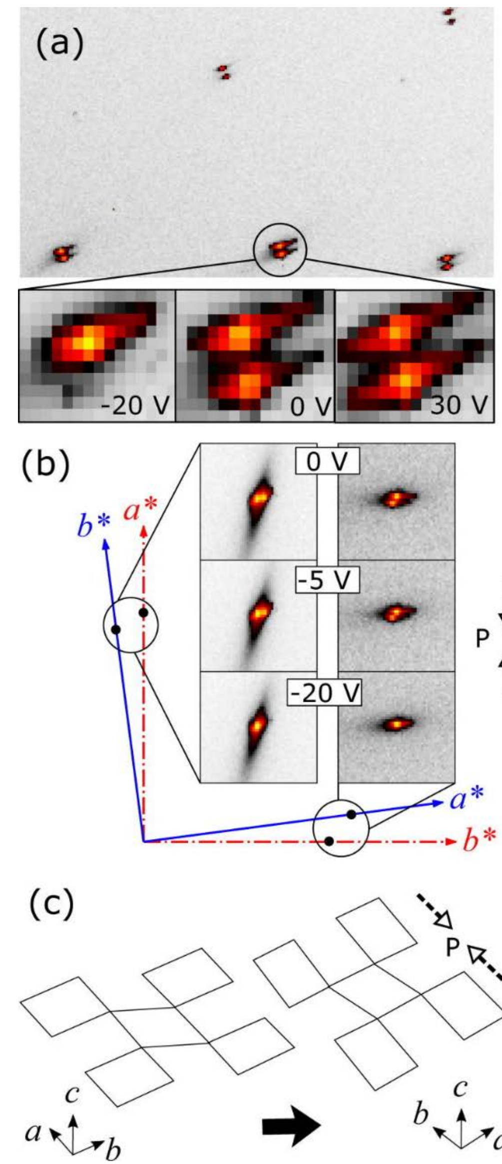
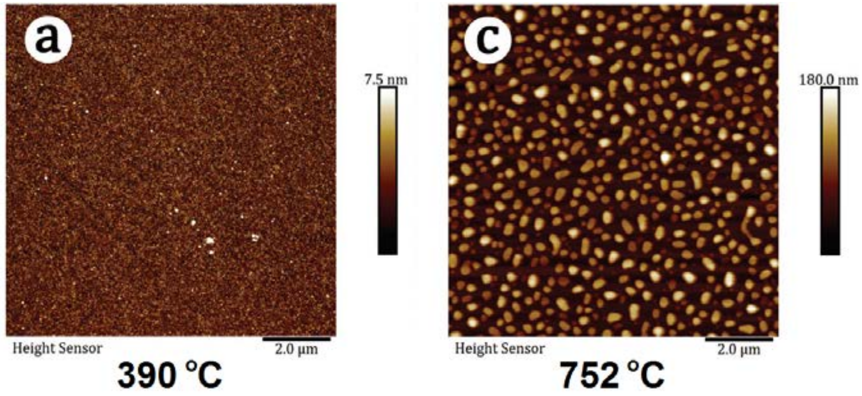
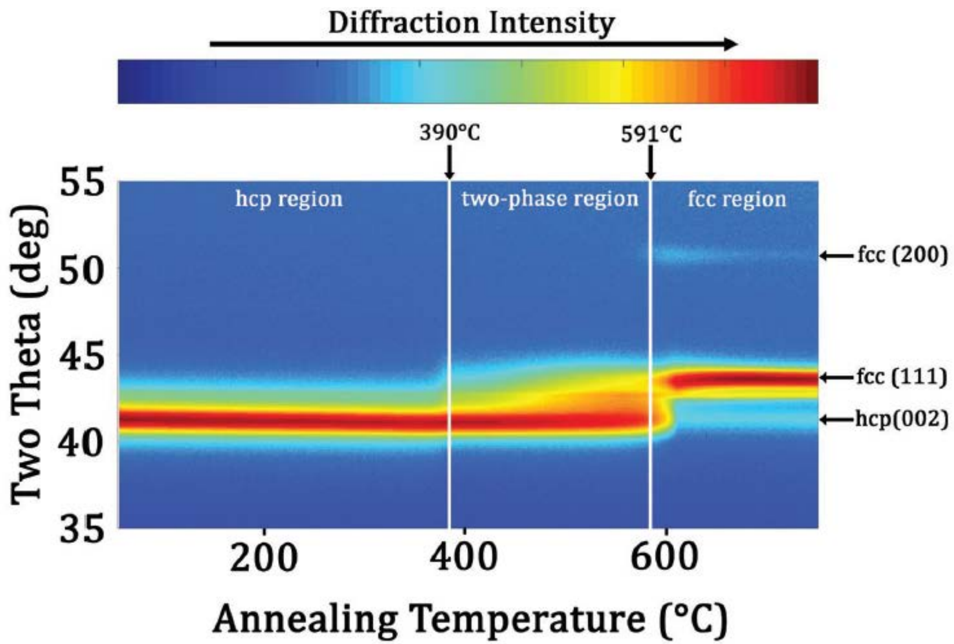
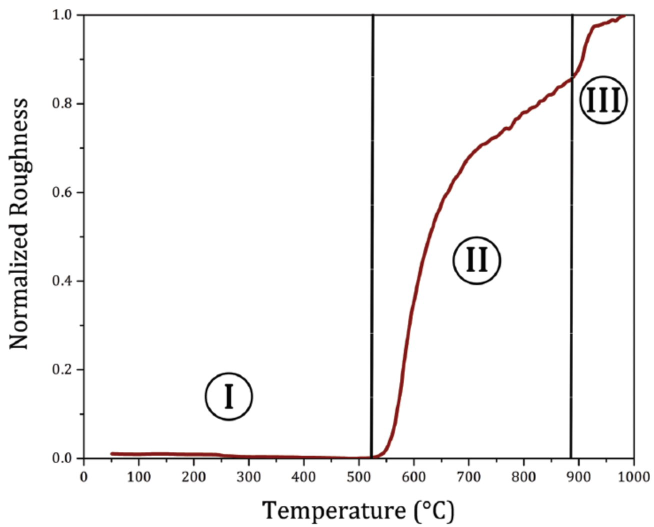


XRD on Thin Films: *In Situ* Phase Transformations

- Temperature dependent phase transformations and growth processes in thin films can be monitored using the IBM endstation on our **IDEAS** beamline.



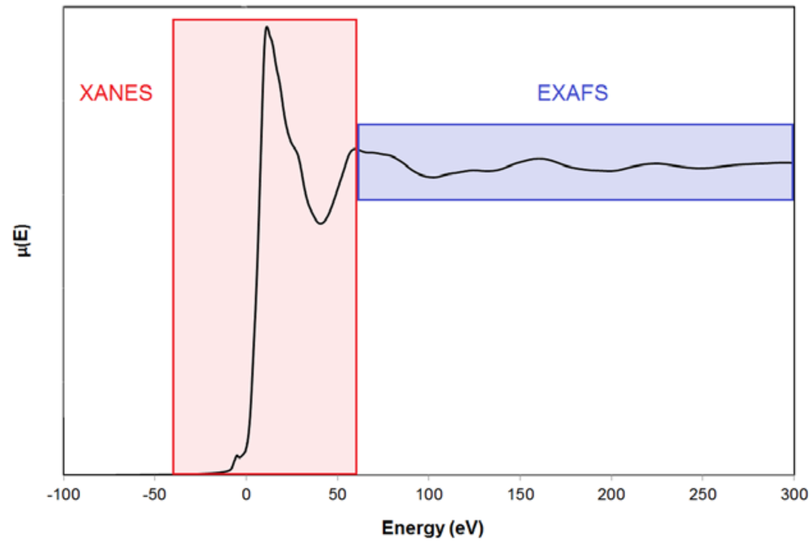


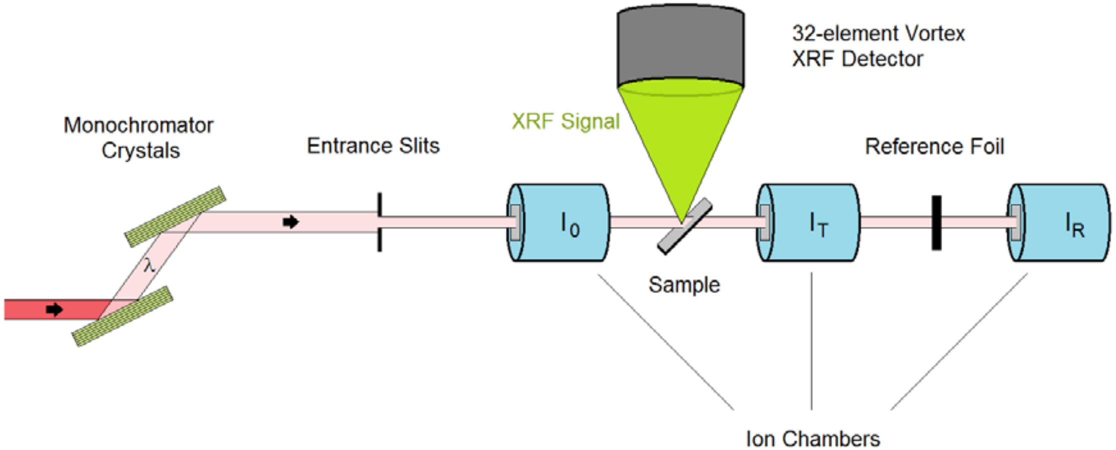


Motamedi, P., *et al*.
Adv. Mater. Interfaces (2018) 1800957

X-ray Absorption Spectroscopy (XAS)

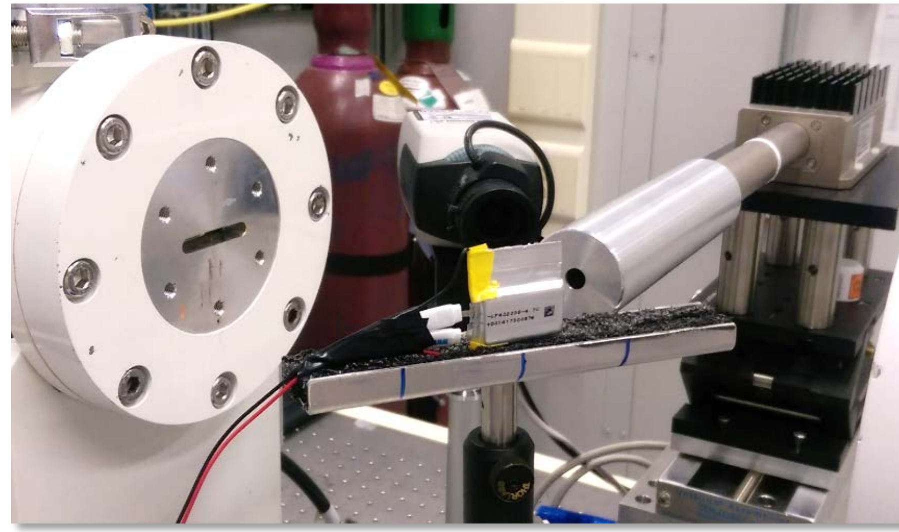
- An XAS spectrum is the result core-shell energy transitions.
- These transitions occur at different energies for different elements, so XAS is an **element-specific** technique.
- XAS is sensitive to bulk **oxidation state** and **local coordination geometry.**
- XAS can be used to carry out **quantitative analysis of chemical species.**



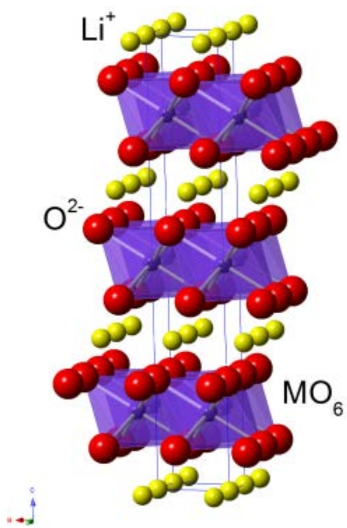


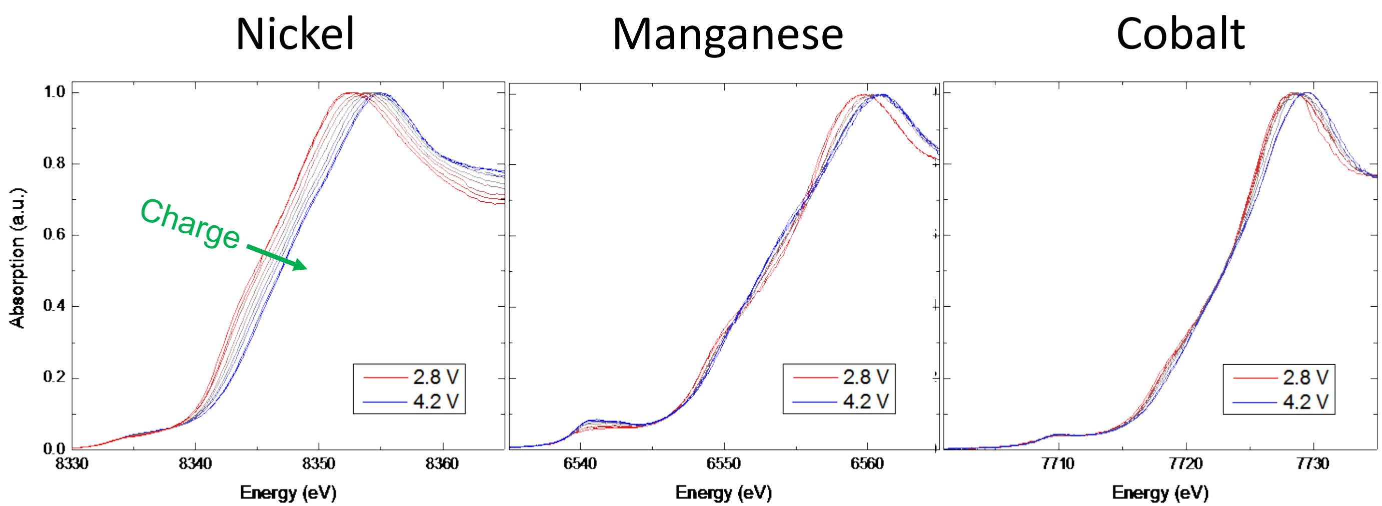
XAS Applications: Charge Compensation in Batteries

- When Li-ion batteries are charged and discharged, the electrode materials are oxidized and reduced.
- Which is the active element?
- XAS can be used *in-situ* to look at each element in the material.



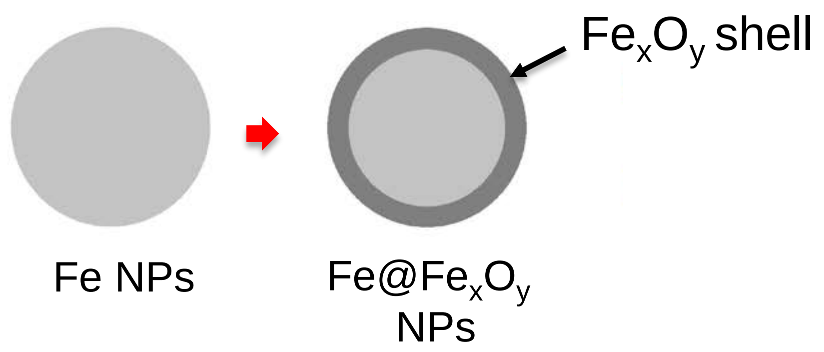
IDEAS beamline





XAS Applications: Developing New Catalysts

- Iron/iron oxide ($Fe@Fe_xO_y$, core@shell) nanoparticles (NPs) make attractive candidates for new catalysts:
  - Iron is abundant, relatively inexpensive and can be magnetically recovered.
  - $Fe@Fe_xO_y$ NPs can be used as catalytic supports, or hollowed out and used to seed the reduction of other metals to form bimetallic NPs.



- XAS is well suited to study both (1) the synthesis of new NPs and (2) their catalytic performance. Recent work has demonstrated this can be performed *in situ*.

Yao, Y., Hu, Y. & Scott, R.W.J. *J. Phys. Chem. C* 118 (2014) 22317-22324.
Yao, Y., Patzig, C., Hu, Y. & Scott, R.W.J. *J. Phys. Chem. C* 119 (2015) 21209-21218.
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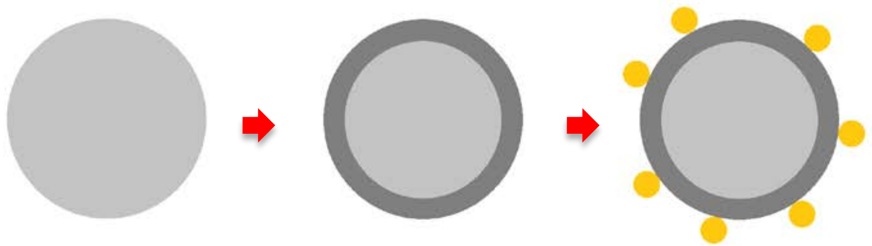
XAS Applications: Developing New Catalysts

- Iron/iron oxide ($Fe@Fe_xO_y$, core@shell) nanoparticles (NPs) make attractive candidates for new catalysts:
  - Iron is abundant, relatively inexpensive and can be magnetically recovered.
  - $Fe@Fe_xO_y$ NPs can be used as catalytic supports, or hollowed out and used to seed the reduction of other metals to form bimetallic NPs.



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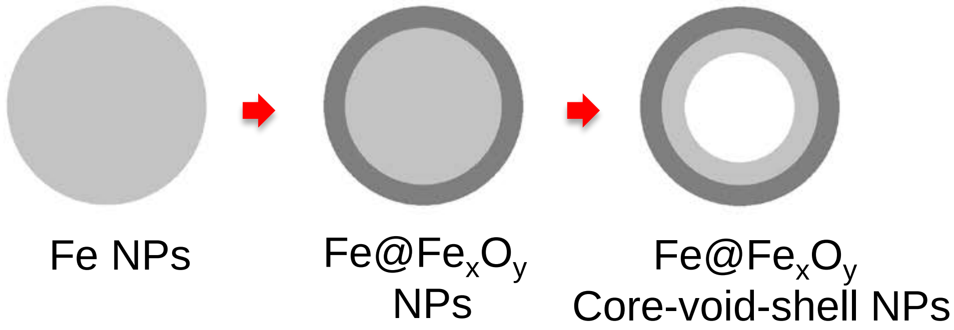

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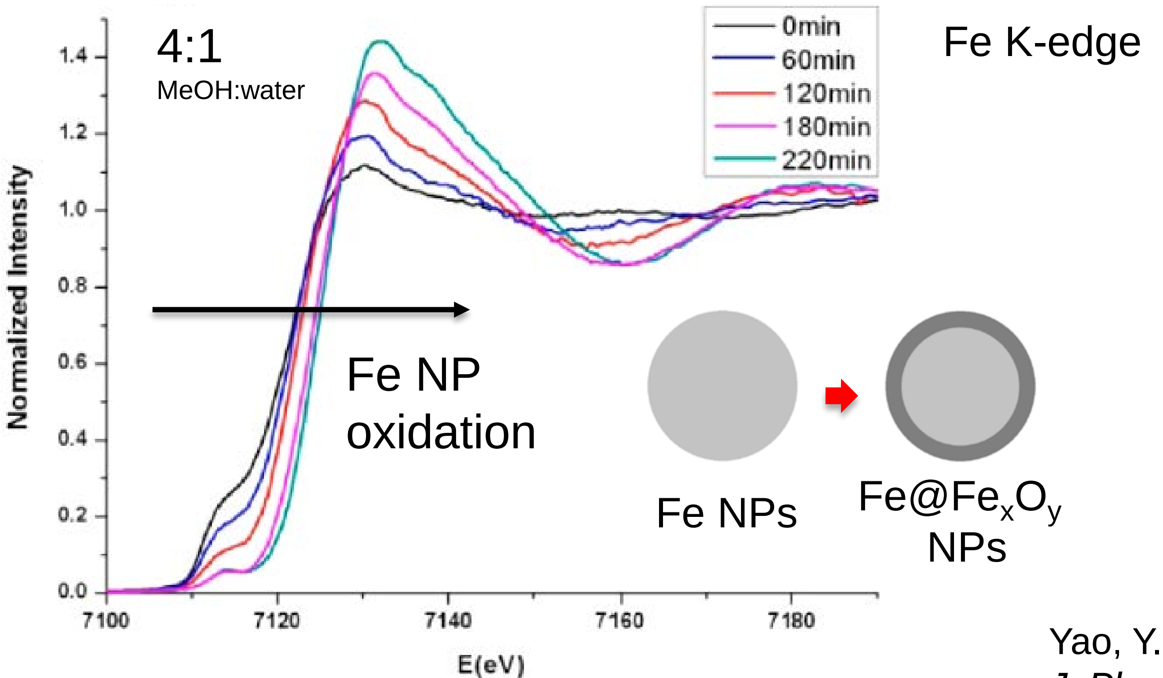
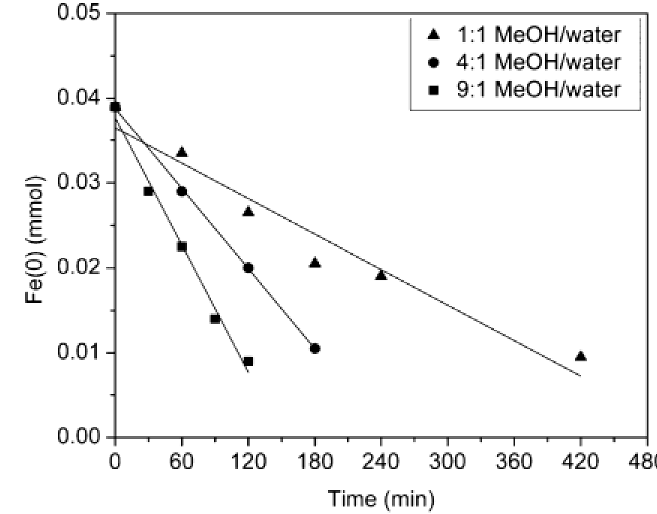
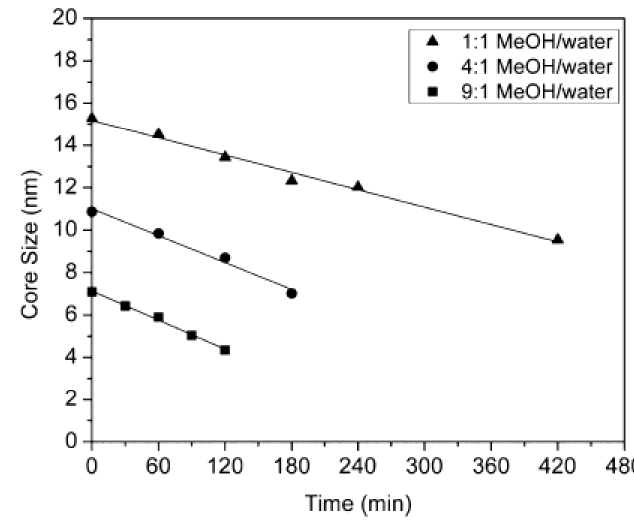
Yao, Y., Patzig, C., Hu, Y. & Scott, R.W.J. *J. Phys. Chem. C* 121 (2017) 19735-19742.

Synthesizing Fe@Fe_xO_y Nanoparticles

- Controlled oxidation synthesis of Fe@Fe_xO_y NPs can be obtained by tailoring the solvent ratio.
- The kinetics of the Fe NP oxidation reaction can be monitored *in situ* with XANES.





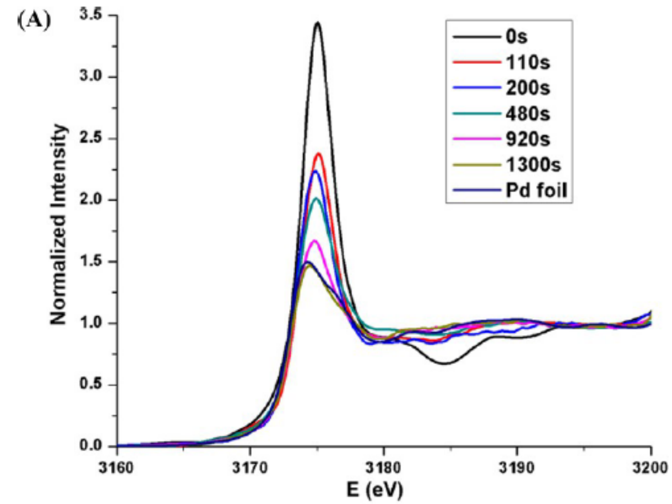


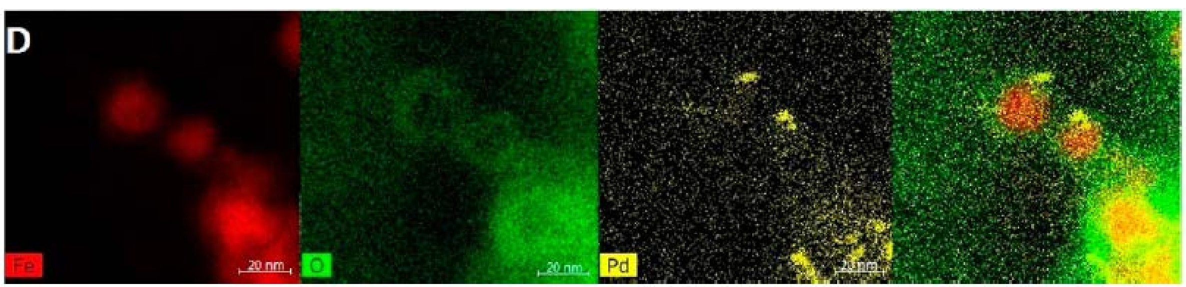
Yao, Y., Hu, Y. & Scott, R.W.J.
J. Phys. Chem. C 118 (2014) 22317-22324.

Fe@Fe_xO_y Supported Pd & Cu Nanoparticles

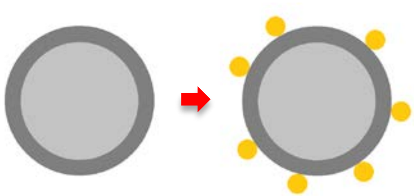
- The performance of Fe@Fe_xO_y NPs for reduction of metals like palladium (shown) and copper from salts in solution can also be studied.

- $Pd(NO_3)_2$ and $CuSO_4$ salts can be fully reduced to Pd^0 and Cu^0 in ~ 20 minutes.



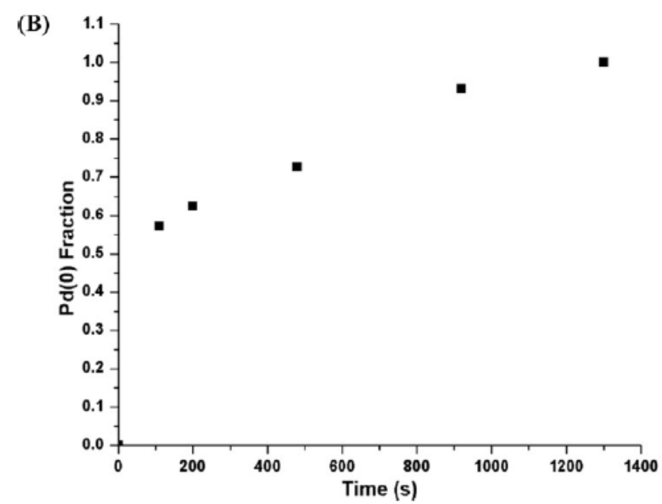


20 nm



Fe@Fe_xO_y NPs

Fe@Fe_xO_y Supported Pd



Yao, Y., Patzig, C., Hu, Y. & Scott, R.W.J. *J. Phys. Chem. C* 119 (2015) 21209-21218.

$Fe@Fe_xO_y$ Supported Pd & Cu Nanoparticles

- The performance of $Fe@Fe_xO_y$ NPs for reduction of metals like palladium (shown) and copper from salts in solution can also be studied.

- EXAFS can be used to look at the local structure of the Pd, including the first shell coordination number (CN) and nearest neighbor distances.

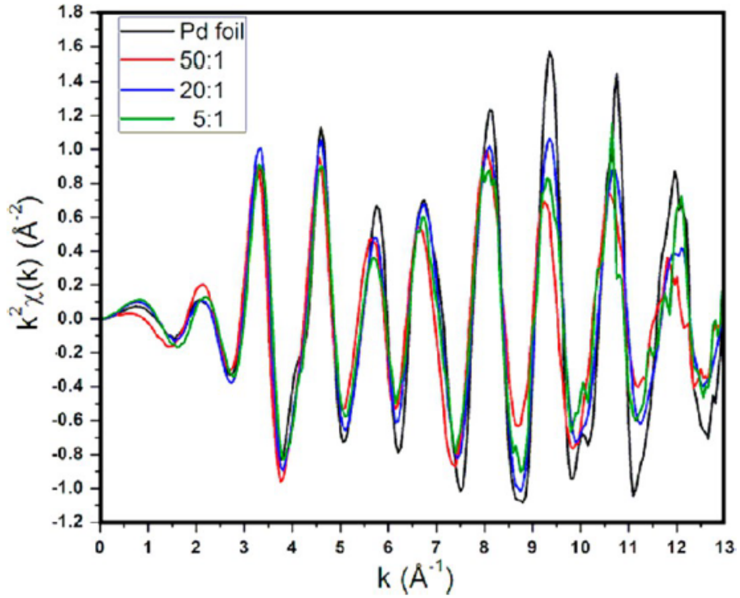
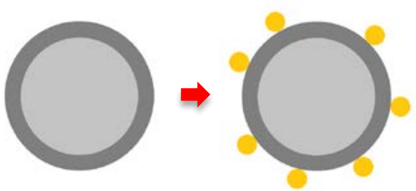


Table 1. Values for the EXAFS Fit of $Fe@Fe_xO_y$/Pd NPs with Different Molar Ratios of $Fe@Fe_xO_y$ NPs to Pd^{2+}

Fe:Pd ratio	shell	CN[a]	R (Å)	σ^2 (Å)	ΔE_0 (eV)
50:1	Pd–Pd	10.3 (9)	2.755 (4)	0.010 (1)	3.3 (6)
20:1	Pd–Pd	10.0 (9)	2.74 (1)	0.008 (1)	3.5 (5)
5:1	Pd–Pd	9.3 (0.8)	2.752 (1)	0.009 (1)	5.1 (5)

[a]First shell coordination number.

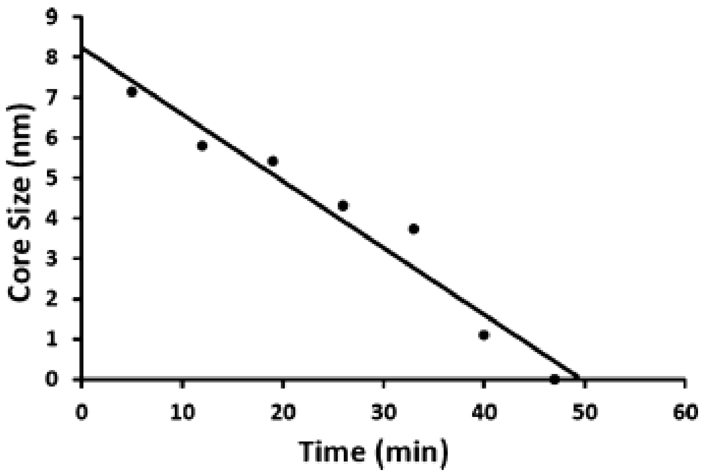


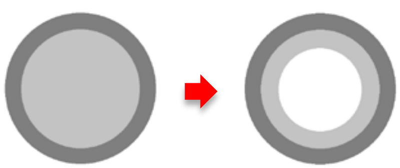
$Fe@Fe_xO_y$ NPs → $Fe@Fe_xO_y$ Supported Pd

Yao, Y., Patzig, C., Hu, Y. & Scott, R.W.J. *J. Phys. Chem. C* 119 (2015) 21209-21218.

Synthesizing Hollow Fe@Fe_xO_y Nanoparticles

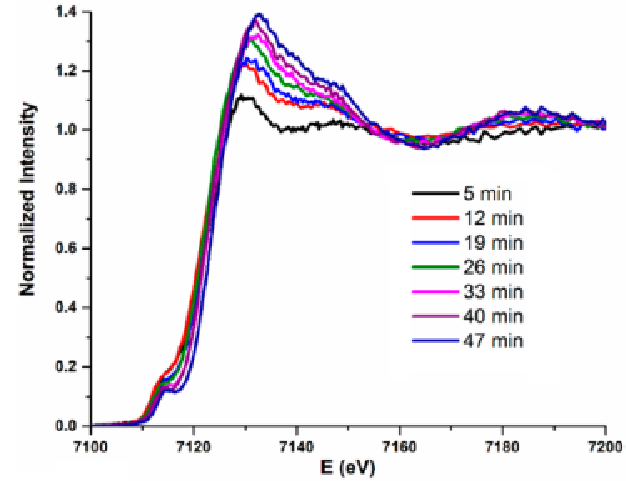
- Synthesis of Fe@Fe_xO_y core-void-shell NPs via the Kirkendall effect can be monitored *in situ* at 180°C using a high temperature liquid cell.

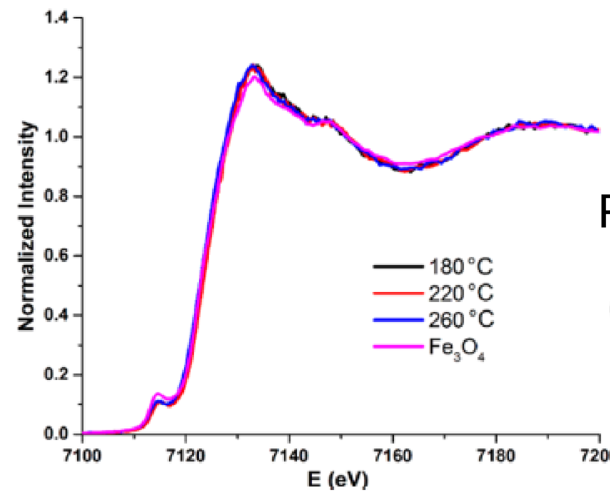




Fe@Fe_xO_y NPs

Fe@Fe_xO_y Core-void-shell NPs



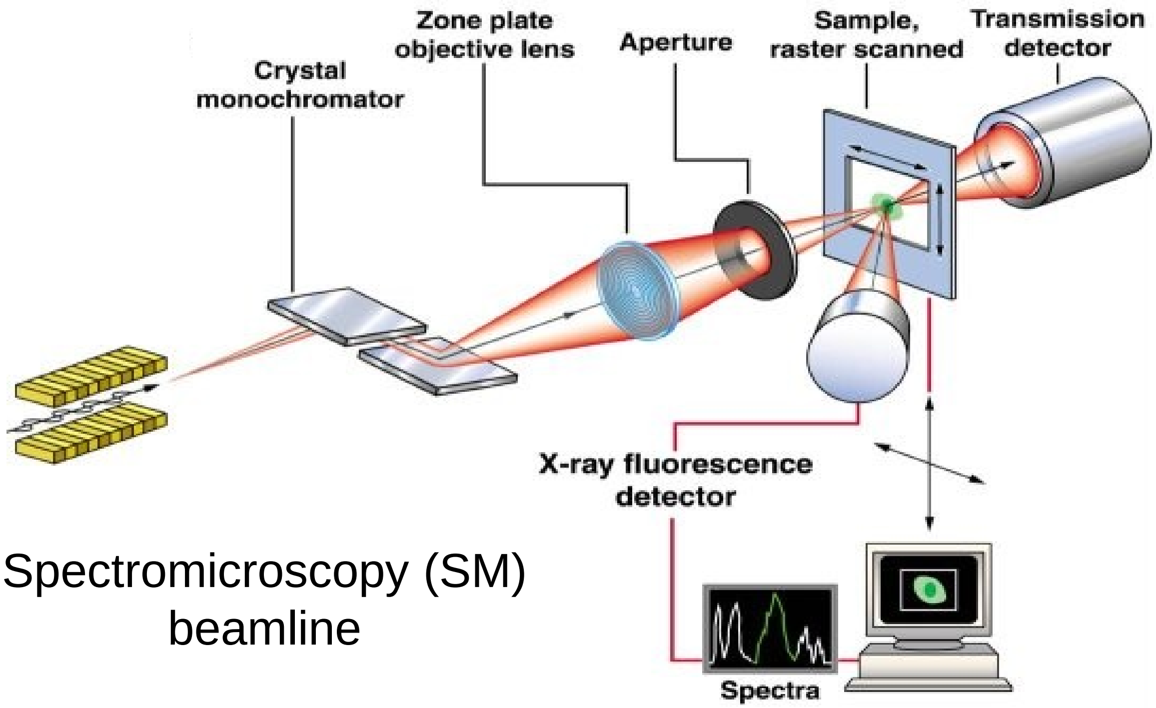


Fe_3O_4

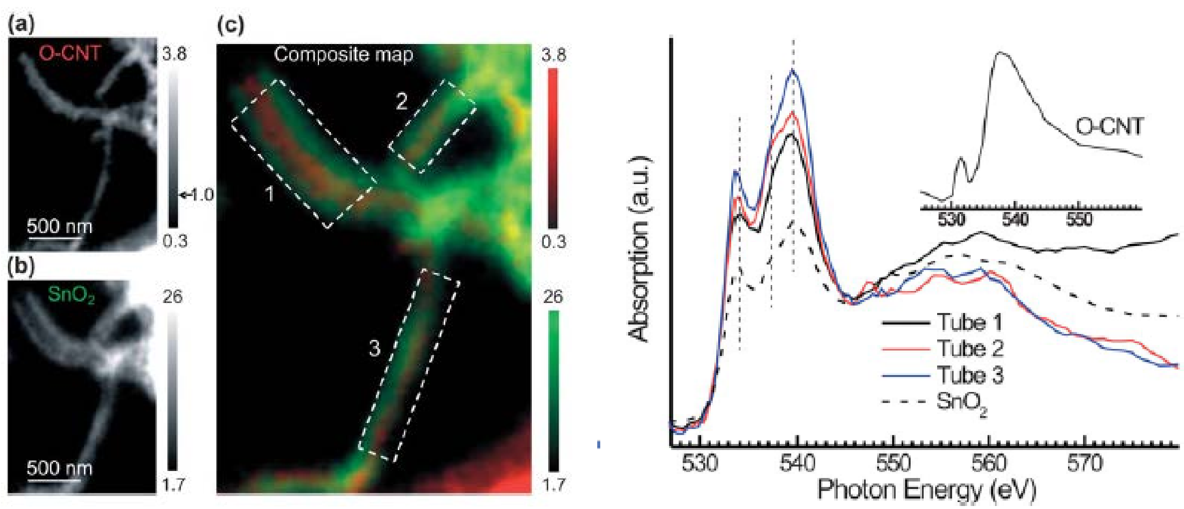
Yao, Y., Patzig, C., Hu, Y. & Scott, R.W.J. *J. Phys. Chem. C* 121 (2017) 19735-19742.

X-ray Spectromicroscopy

- A synchrotron beam can be focused down to a very small spot size (anywhere from 2 mm down to ~30 nm).
- This can be used for elemental mapping.
- It can also be used for chemical mapping.
- The technique illustrated upper right is called scanning tunneling X-ray microscopy (STXM).



Spectromicroscopy (SM) beamline



Zhou, J. *et al.* *J. Phys. Chem. Lett.* 1 (2010) 1709-1713.

Canadian Light Source
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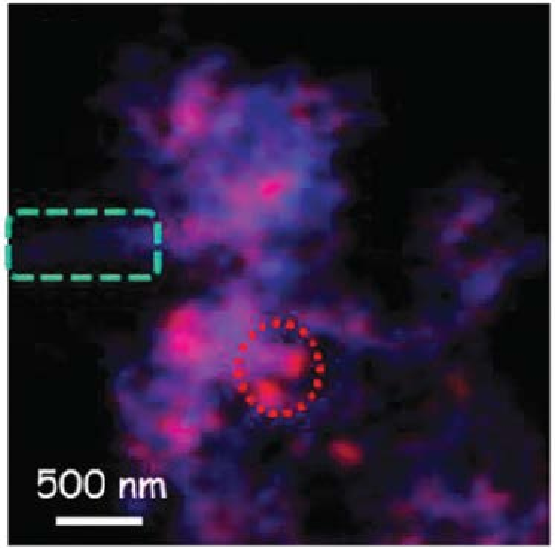
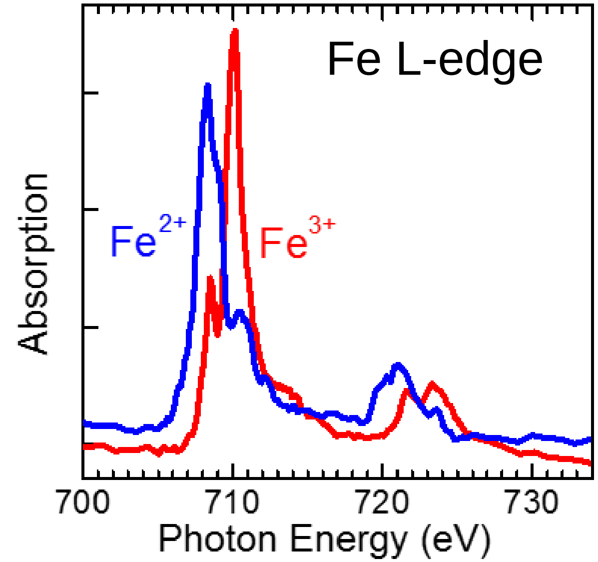
STXM Applications: Charge State in a Battery

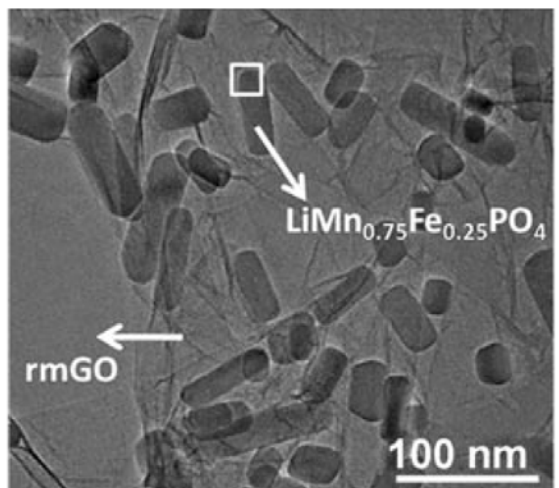
- STXM can be used to image localized iron oxidation states regions in olivine/ graphene composite cathodes.

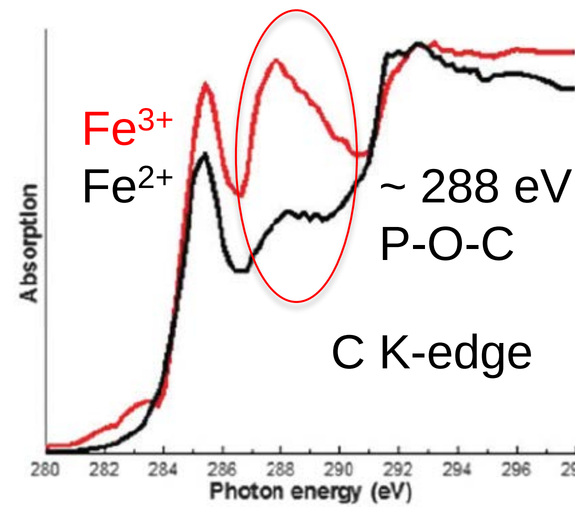
- STXM generates an image "stack" where each pixel contains a spectrum.

- This can be used to separate components using spectral features.





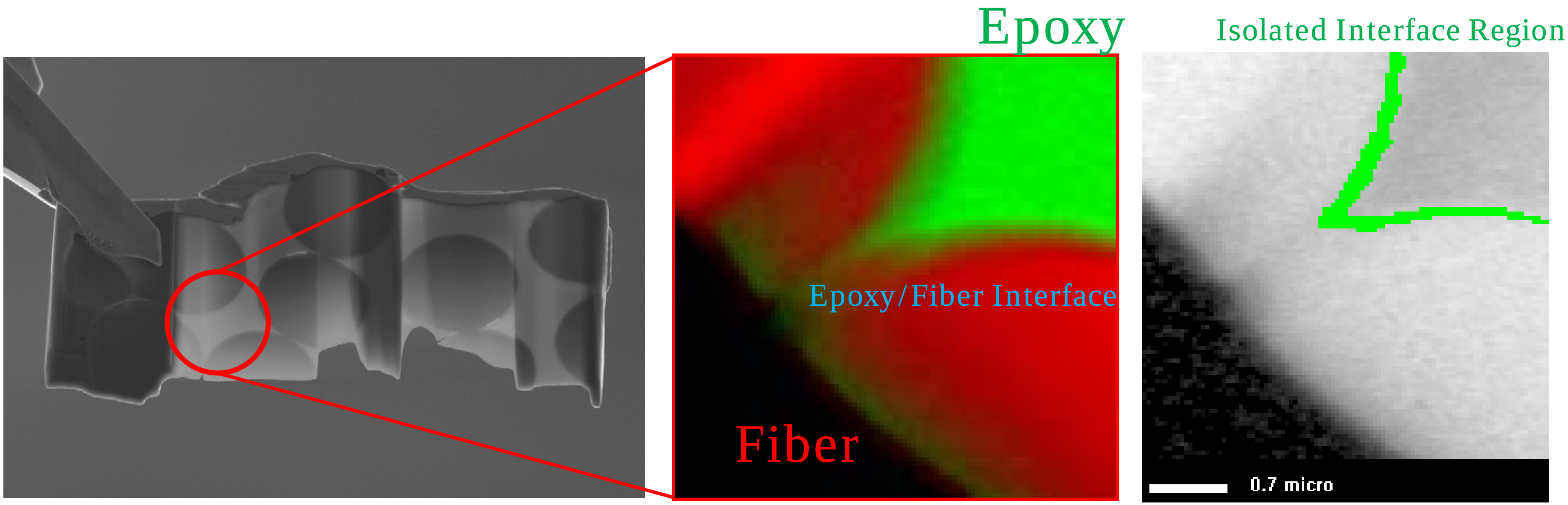




Wang, H. *et al.* *Angew. Chem. Int. Ed.* 50 (2011) 7364-7368.

Zhou, J. *et al. Chem. Commun.* 49 (2013) 1765-1767.

STXM Applications: Interface Studies in Composites

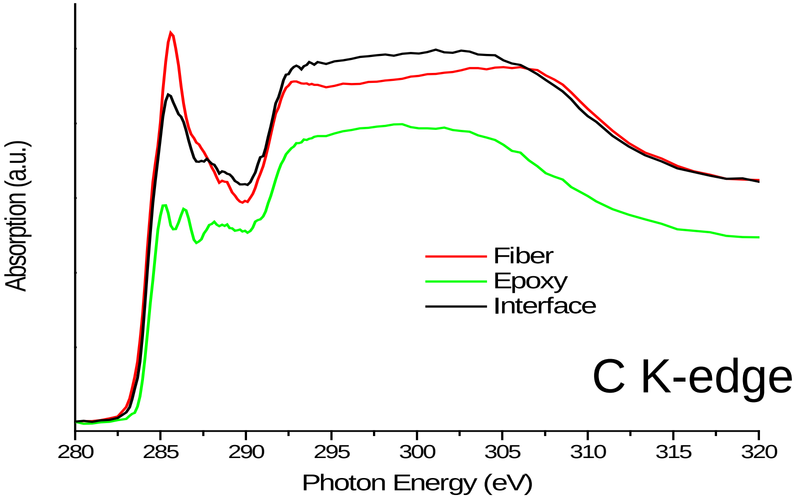


Electron microscope image of carbon fiber cross-section

Synchrotron X-ray microscope image

Interface region highlighted

- A thin section of a unidirectional woven carbon-fiber composite was prepared (synthetic fiber and epoxy-based resin).
- The cross section of the interface was imaged using STXM.



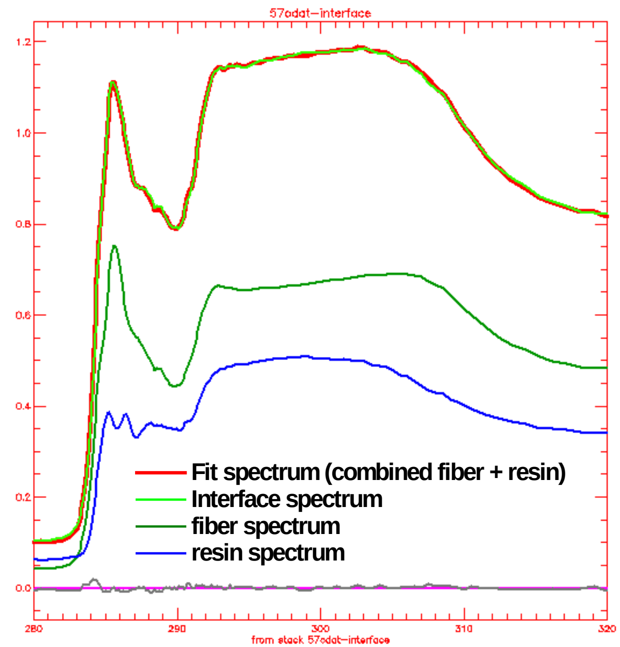
STXM Applications: Interface Studies in Composites

- For **Sample A**, the linear combination of the fiber and resin spectra reproduces the spectrum of the interface region very accurately, indicating that there are **no detectable chemical changes at the interface.**

- For **Sample B**, the best fit of the combined spectrum does not perfectly reproduce the spectrum of the interface region, indicating that there are **chemical interactions involving carbon at the interface.**

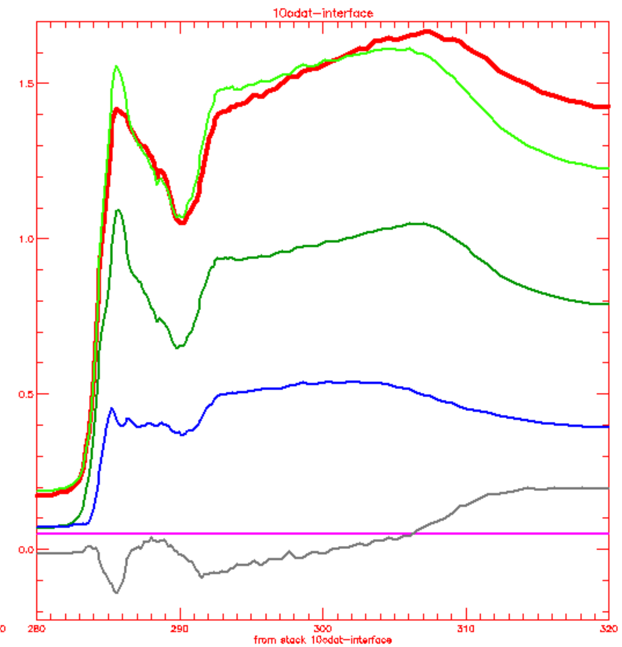
Linear Combination Fits (LCF)

Sample A



55% Fiber
45% Resin

Sample B



58% Fiber
42% Resin

Summary

- The synchrotron is a powerful, multi-purpose tool for materials analysis.

- Synchrotron techniques offers major advantages for:
  - Multi-component and heterogeneous materials.
  - Small sample volumes.
  - *In-situ* and *in-operando* studies.
  - Dilute elements and compounds of interest.

Acknowledgements

- **Our CLS Industrial Science and Science Teams:**
  - Danielle Veikle, David Muir, Denis Spasyuk, Erika Bergen, Jeff Cutler, Jeff Warner, Jian Wang, Jigang Zhou, Renfei Feng, Toby Bond & Yongfeng Hu.

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- Thank you to Professor Robert Scott and his group in Chemistry at the University of Saskatchewan for use of the XAS catalysis examples.

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