CLS XRD Summer School,
August 2022

In-situ diffraction

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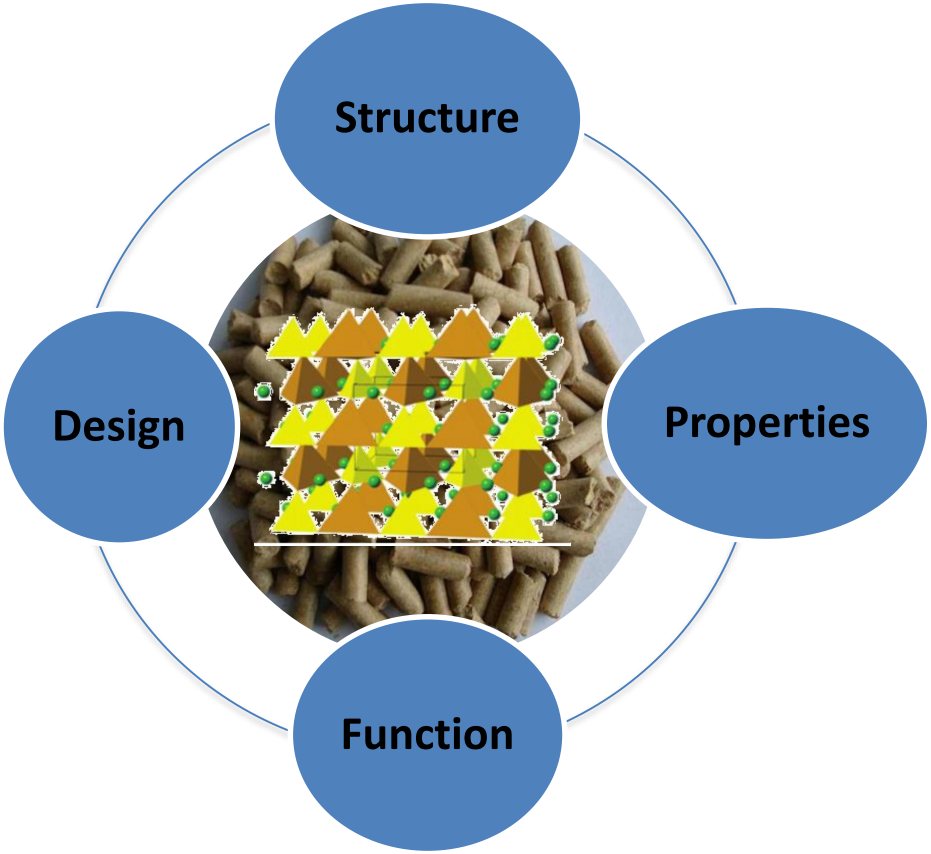
In-situ diffraction Motivation

Studying material under working conditions:

1. temperature
2. atmosphere
3. pressure
4. stress/strain
5. voltage/current
6. Light
7. …

Provides information on the chemical and physical properties of materials and devices under realistic processing conditions



Structure

Properties

Function

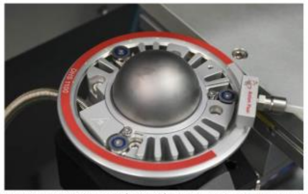
Design

<u>Applications</u>: Microelectronics, batteries and fuel cells, catalysis, solar cells, materials under extreme conditions, etc.

Sample environments

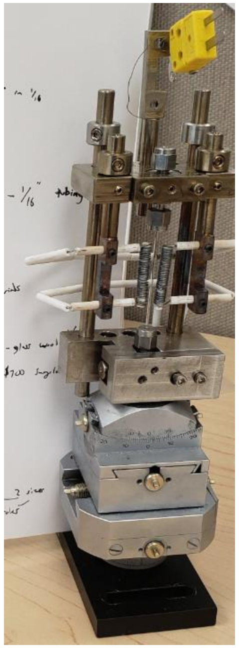
Sample environments seek to mimic the operation conditions of the materials or devices being tested

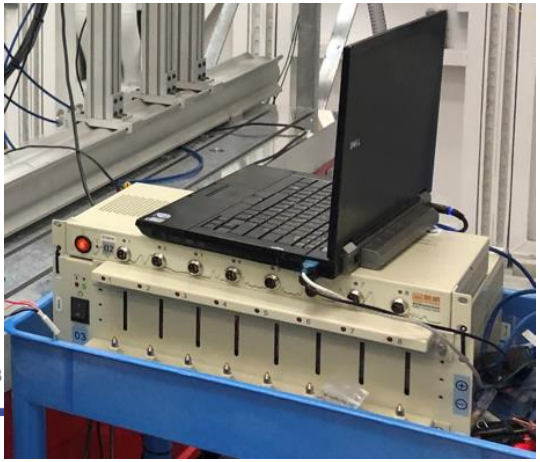
- Furnaces with controlled atmosphere and temperature
- Tensile rigs
- Temperature/humidity light chambers
- in situ cycling / temperature control for battery studies
- Customized setups



The Anton Paar domed heating stage (DHS1100) can be used to heat flat plate samples from ambient temperature to 1100 °C in a variety of inert gas atmospheres or under vacuum.

A Stoe capillary furnace can heat capillaries up to 1770K. Quartz capillaries can be used up to 1370 K, above which sapphire capillaries must be used. Users must supply their own sapphire capillaries.





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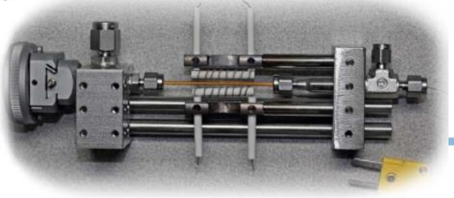


THE B

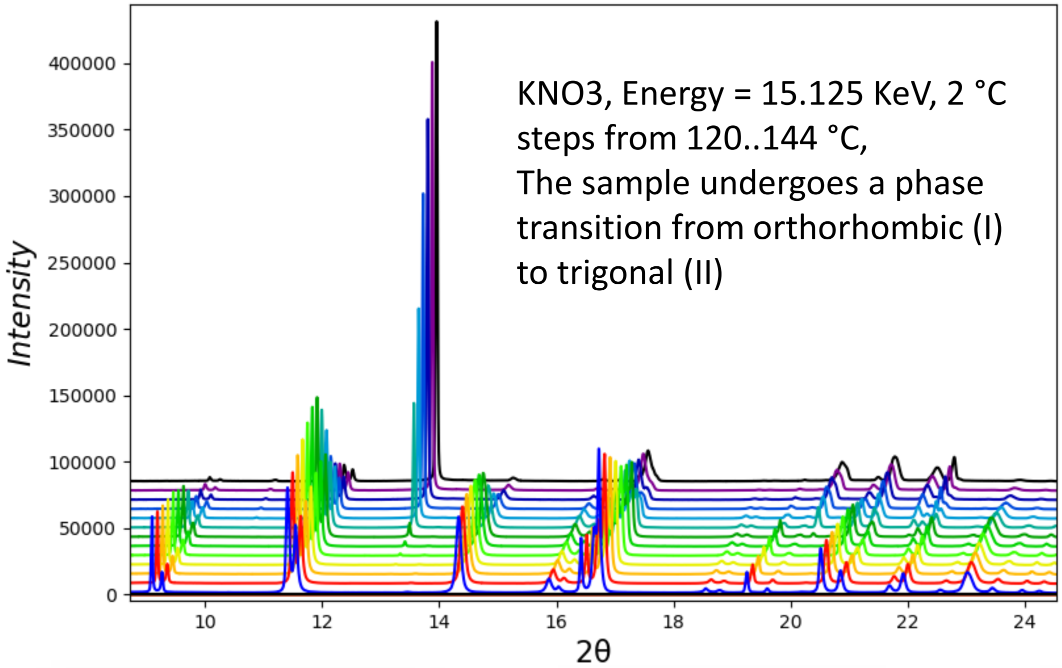
Canadian Light Source Centre canadien de rayonnement synchrotron

Contents

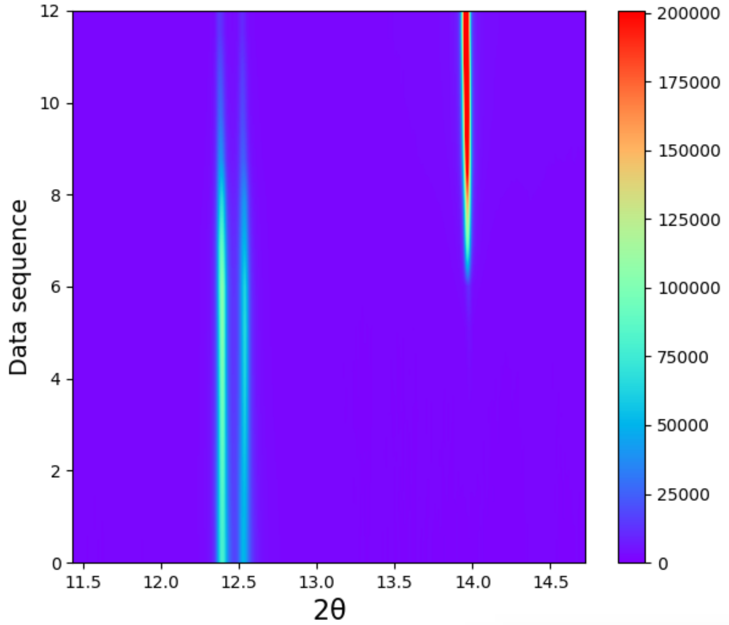
1. Phase transitions
2. Microelectronics
3. Batteries
4. Solar cells
5. Mechanical rigs
6. Catalysts
7. Corrosion
8. High pressure

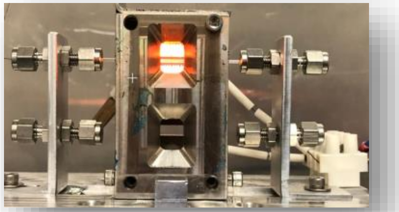
Applications – Structural phase transitions

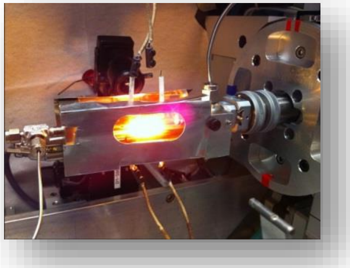
Orthorhombic $\alpha - KNO_3$ to trigonal β - KNO_3 *phase transition*



KNO3, Energy = 15.125 KeV, 2 °C steps from 120..144 °C,
The sample undergoes a phase transition from orthorhombic (I) to trigonal (II)







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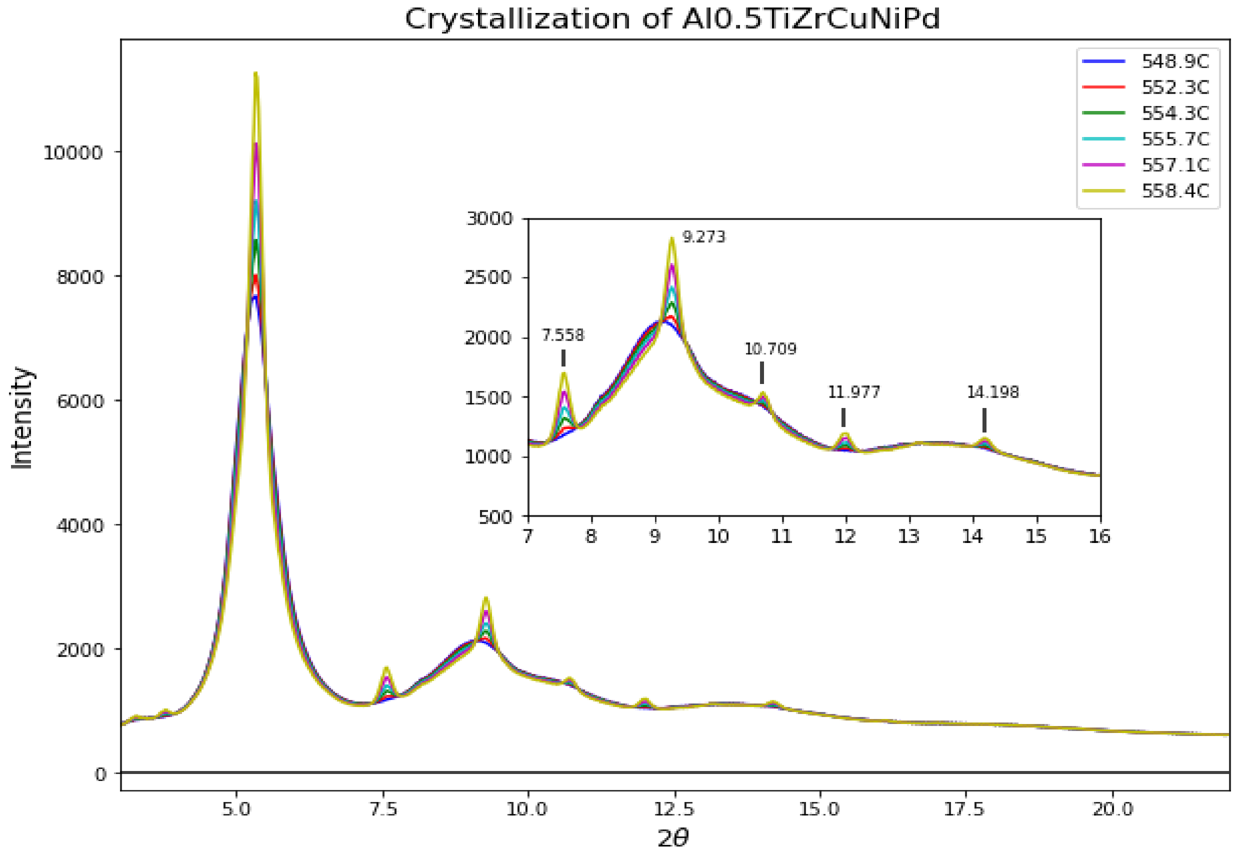
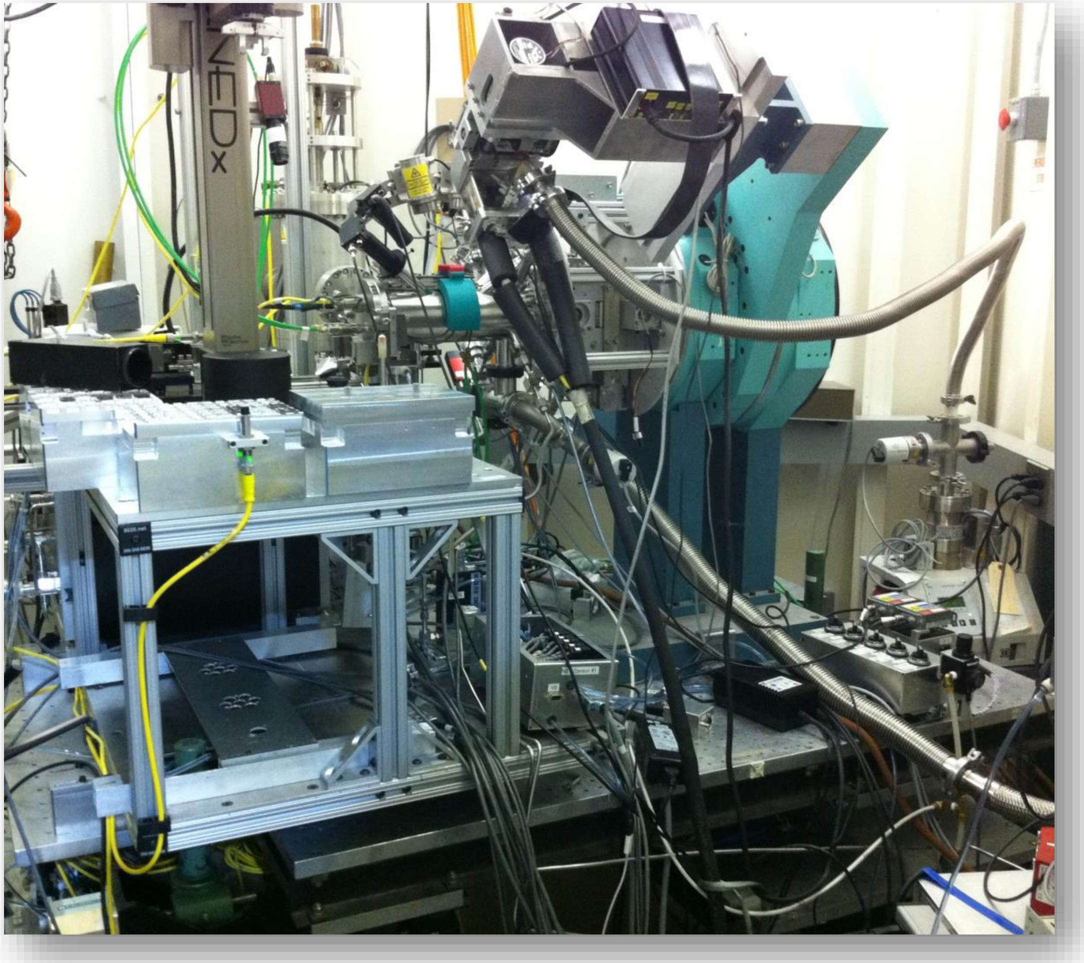
High entropy alloys phase transitions



Applications to Microelectronics

IBM end-station

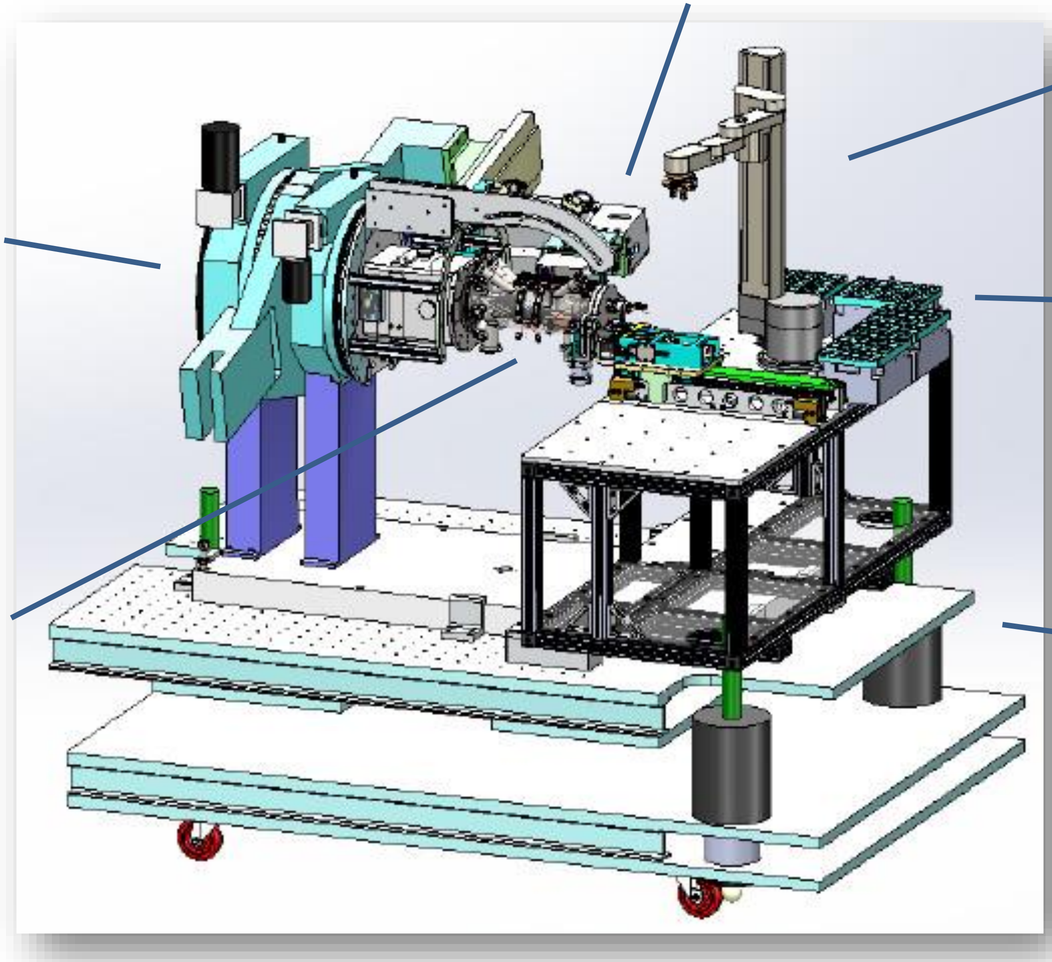


- **In-situ characterization**
  - thin films
  - microelectronic materials
  - semiconductors
- **Rapid thermal annealing (up to ~ 1100°C)**

Techniques

- ✓ X-Ray diffraction
- ✓ Four point probe to measure film resistivity
- ✓ Optical light scattering to measure surface morphology

IBM end-station



Detector

Robot

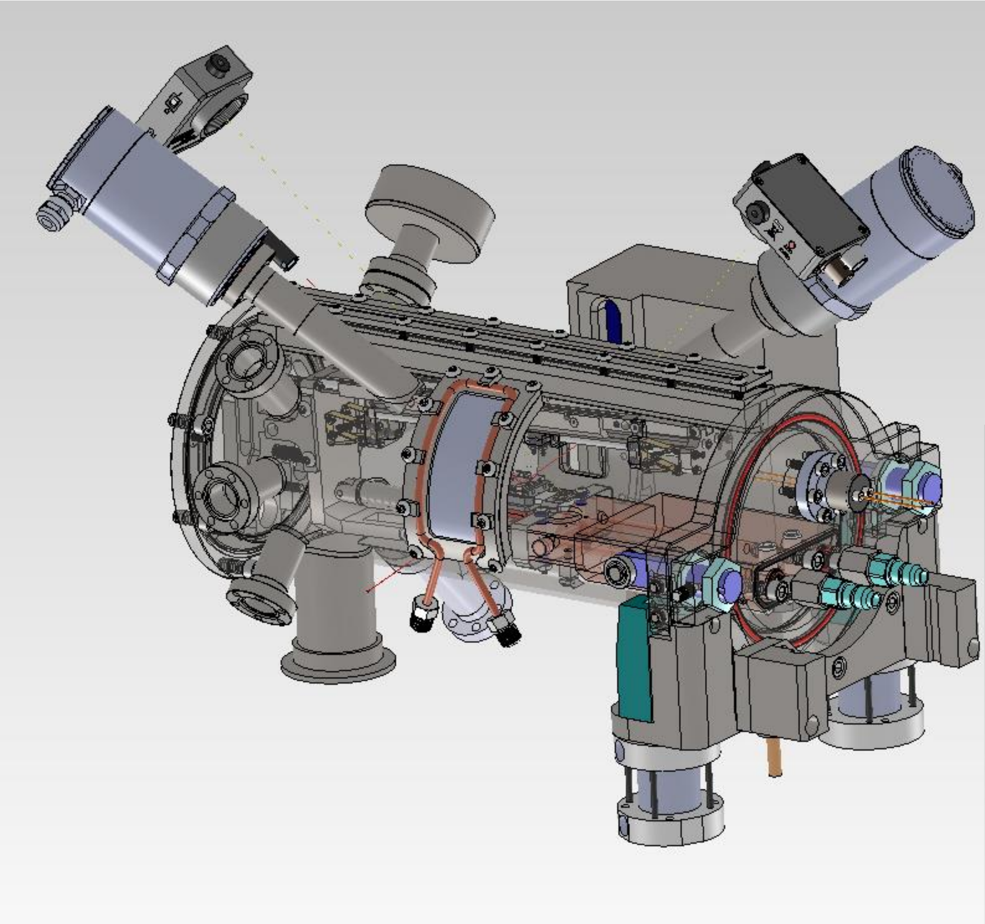
Huber diffractometer

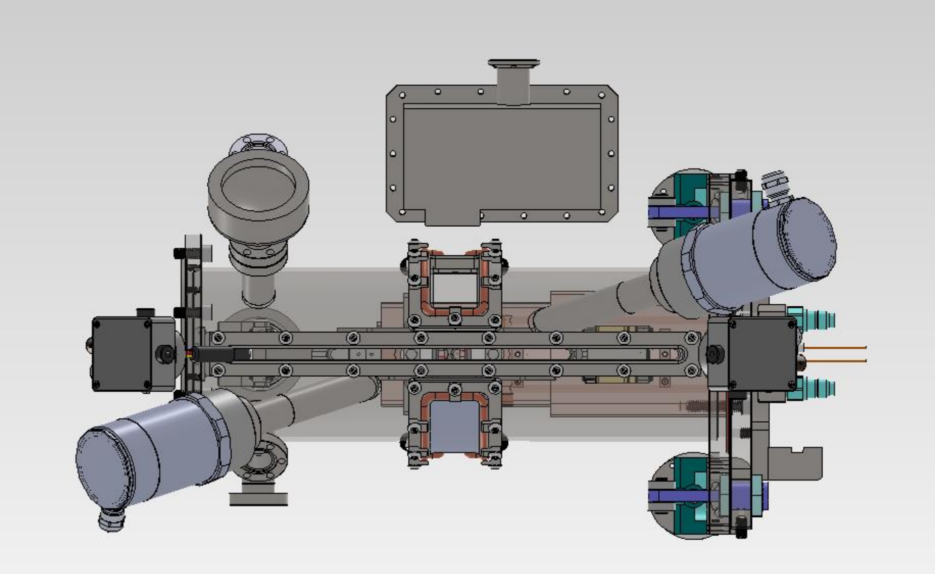
Sample magazines

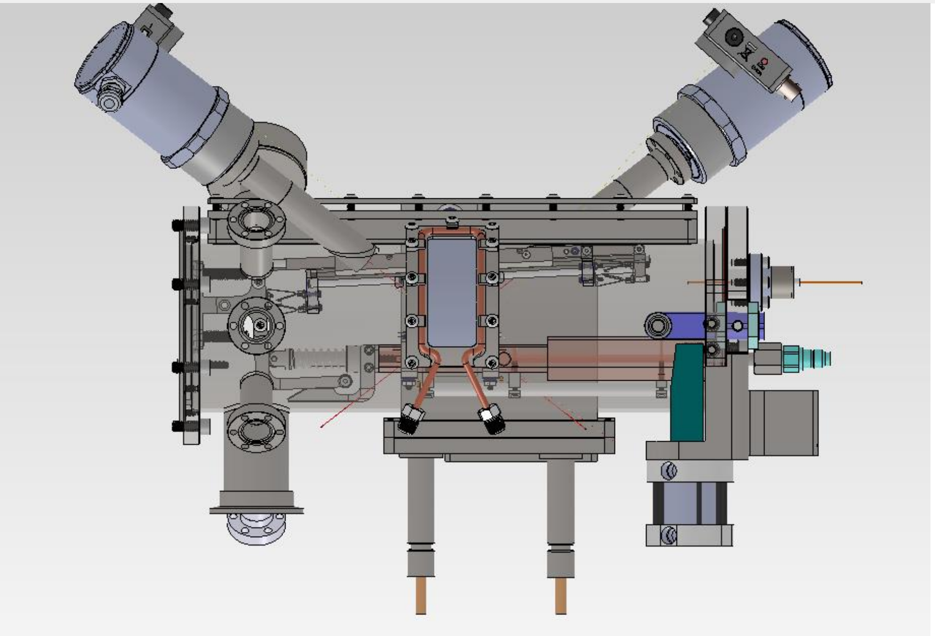
Experiment chamber

Support table

Experiment chamber



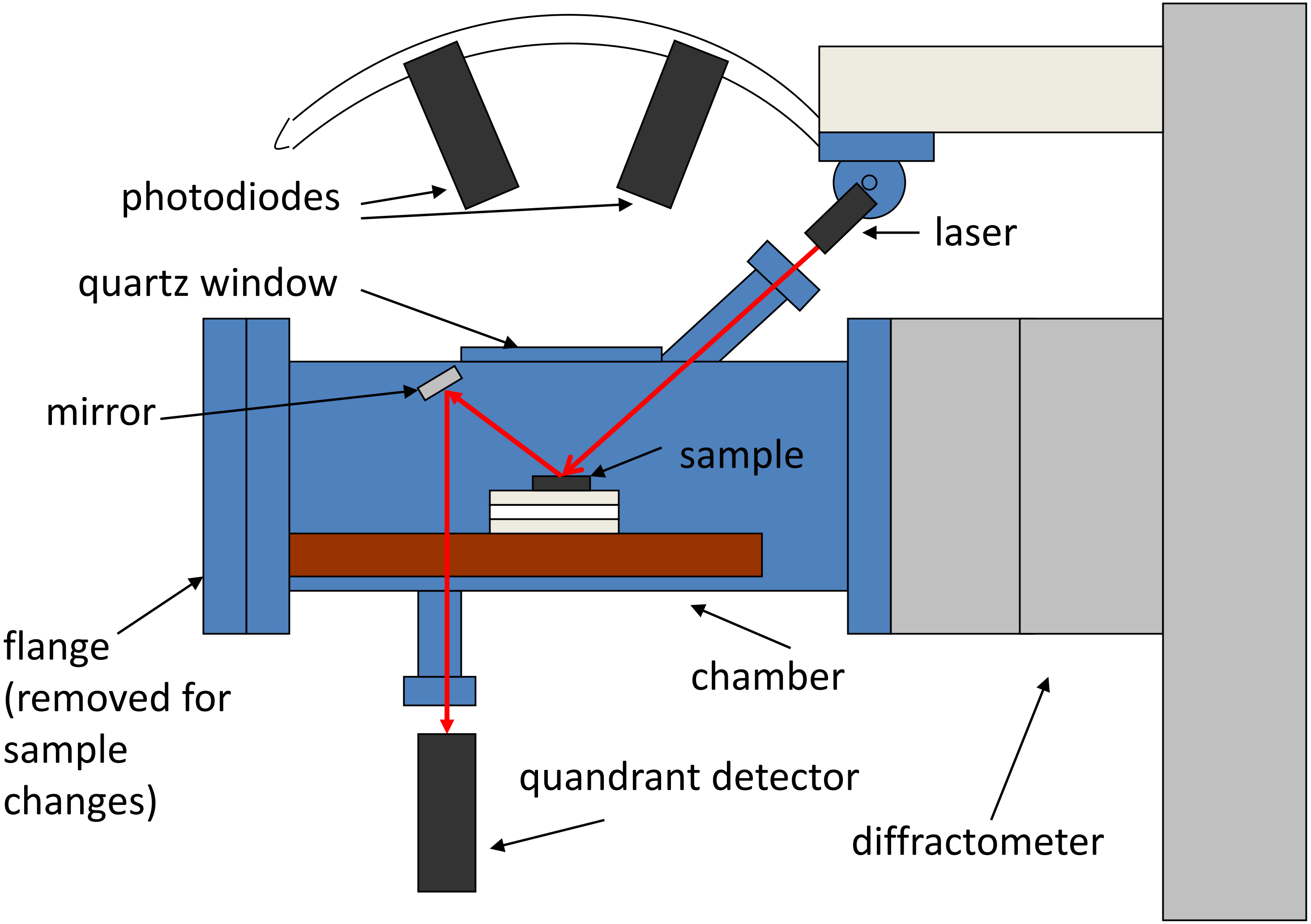




Canadian
Light
Source

Centre canadien
de rayonnement
synchrotron

Experiment chamber



photodiodes

quartz window

mirror

sample

laser

flange (removed for sample changes)

chamber

quandrant detector

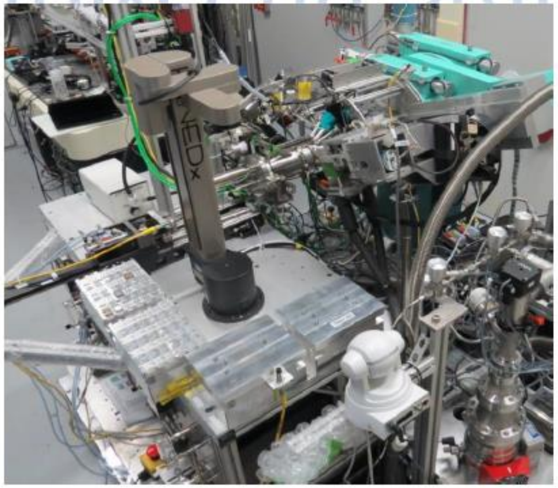
diffractometer

Sample size and format

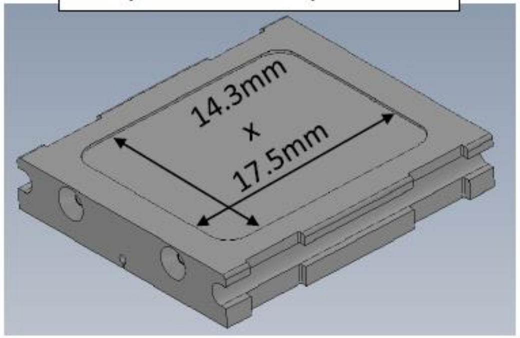
IBM end-station

Thin films studies

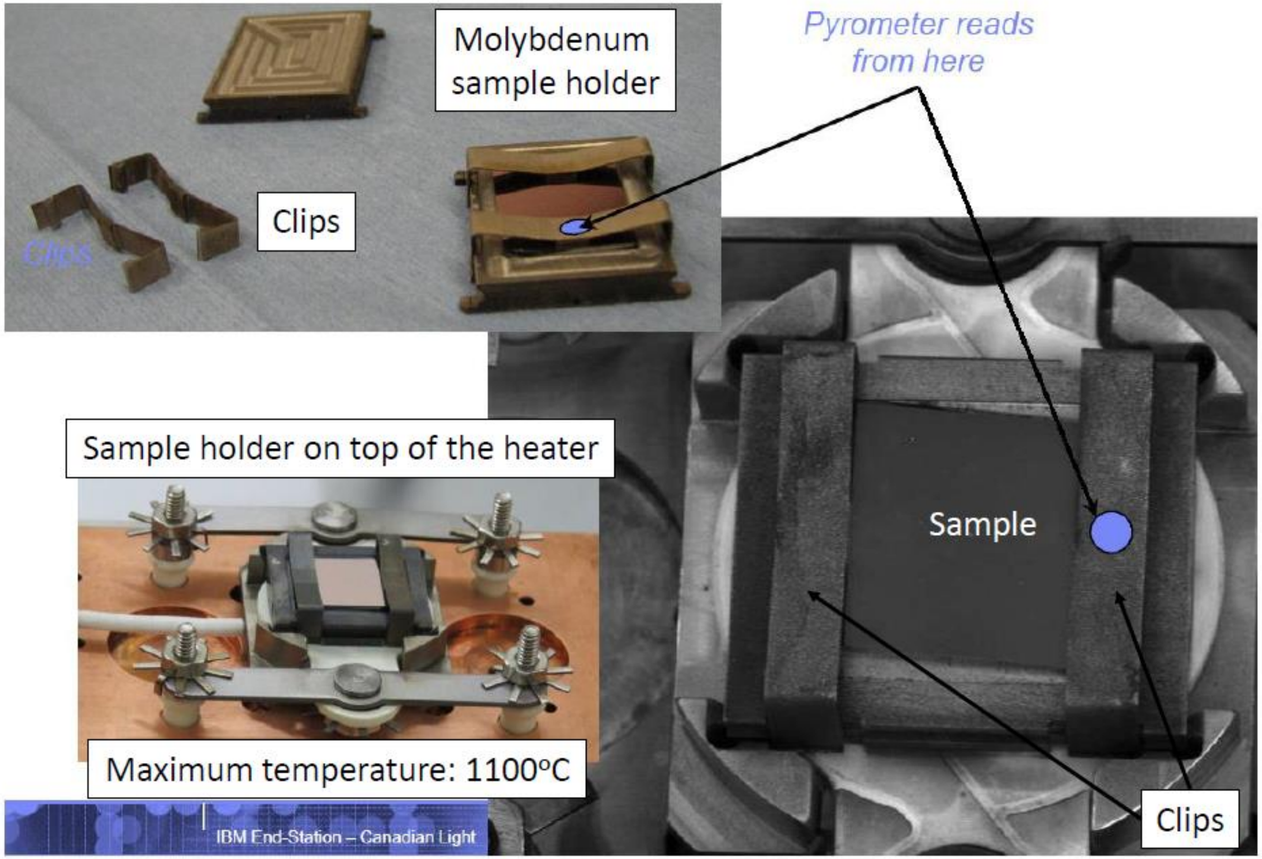
Combined diffraction,
resistivity and roughness measurements
under ultra high purity N_2 or He.
Temperature up to 1100 °C.



Molybdenum sample holder

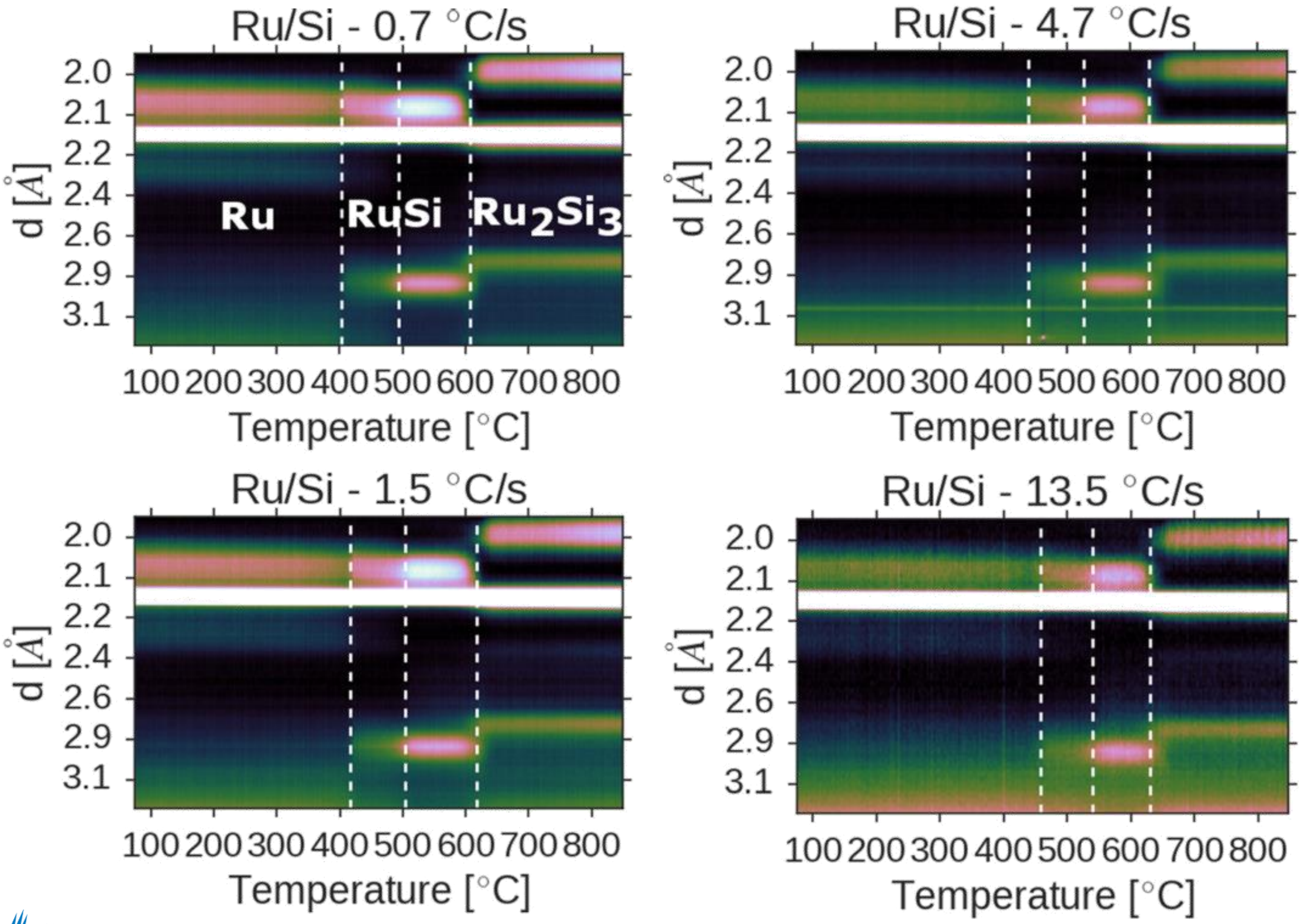


Sample size should be
approximately 12mm x 15 mm



IBM end-station in action

Atomic layer deposited ultrathin metal nitride barrier layers for ruthenium interconnect applications. Sonal Dey et al.



Journal of Vacuum Science & Technology A **35**, 03E109 (2017)

IBM end-station

Effects of additive elements on the phase formation and morphological stability of nickel monosilicide films

- ✓ Quick investigation of different growth conditions
- ✓ Better nucleation processes
- ✓ Improved film stability at higher temperatures
- ✓ Lower interface roughness

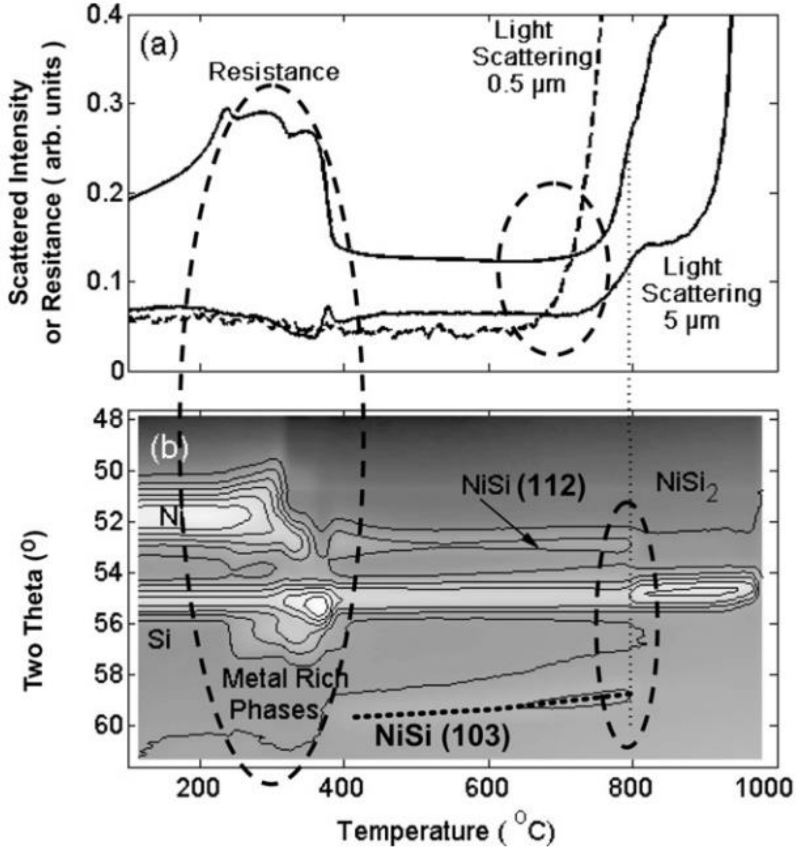


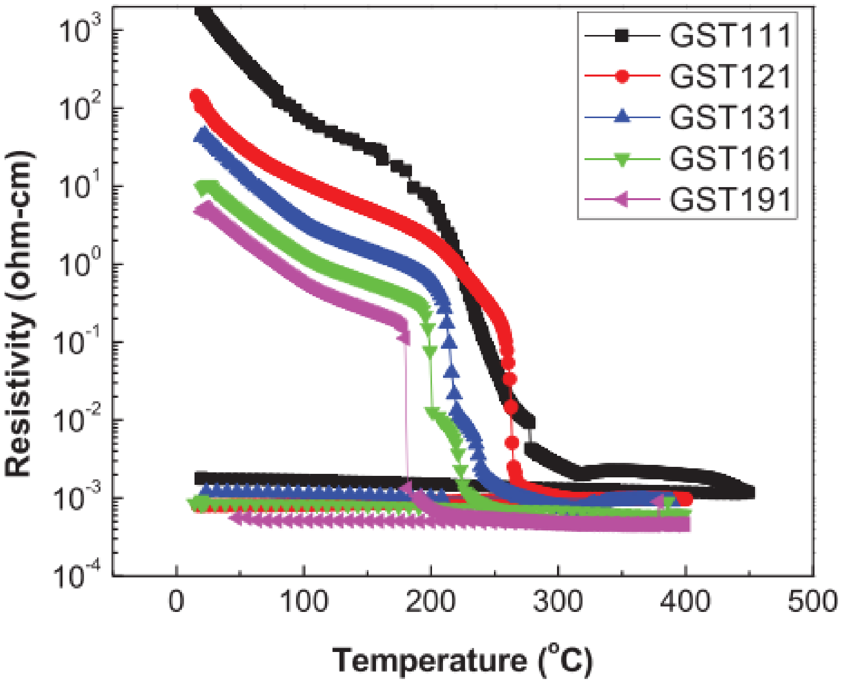
Fig. 4. (a) Elastic light scattering at 0.5 µm and 5 µm length scales and resistance measurements together with (b) X-ray diffraction measurements performed *in situ* during annealing in purified He of a 15 nm Ni layer deposited on a 100 nm poly-Si film (3 °C /s). The three ellipse also refer to the challenges discussed using the phase diagram in Fig. 1.

Microelectronic Engineering
83, 2042-2054 (2006)

C. Lavoie et al.

IBM end-station

Crystallization properties of materials along the pseudo-binary line between GeTe and Sb



Resistivity as a function of temperature for $Ge_1Sb_xTe_1$ films for $x > 1$ during a heating ramp to 300–450 °C at 5 °C/min and subsequent cooling back to room temperature.

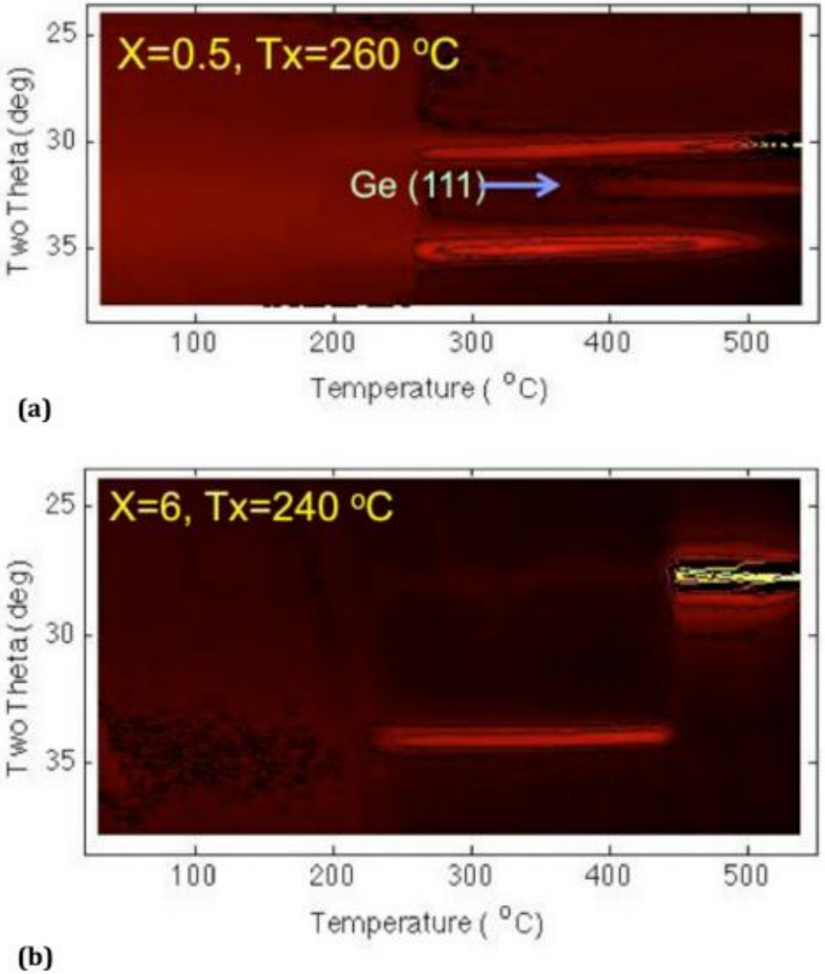


FIG. 2. XRD peak intensity as a function of temperature T during heating at 3 °C/s to 550 °C of a $Ge_1Sb_xTe_1$ film with (a) $x = 0.5$ and (b) $x = 6$, respectively.

Journal of Applied Physics **115**, 093101 (2014)
Huai-Yu Cheng et al.

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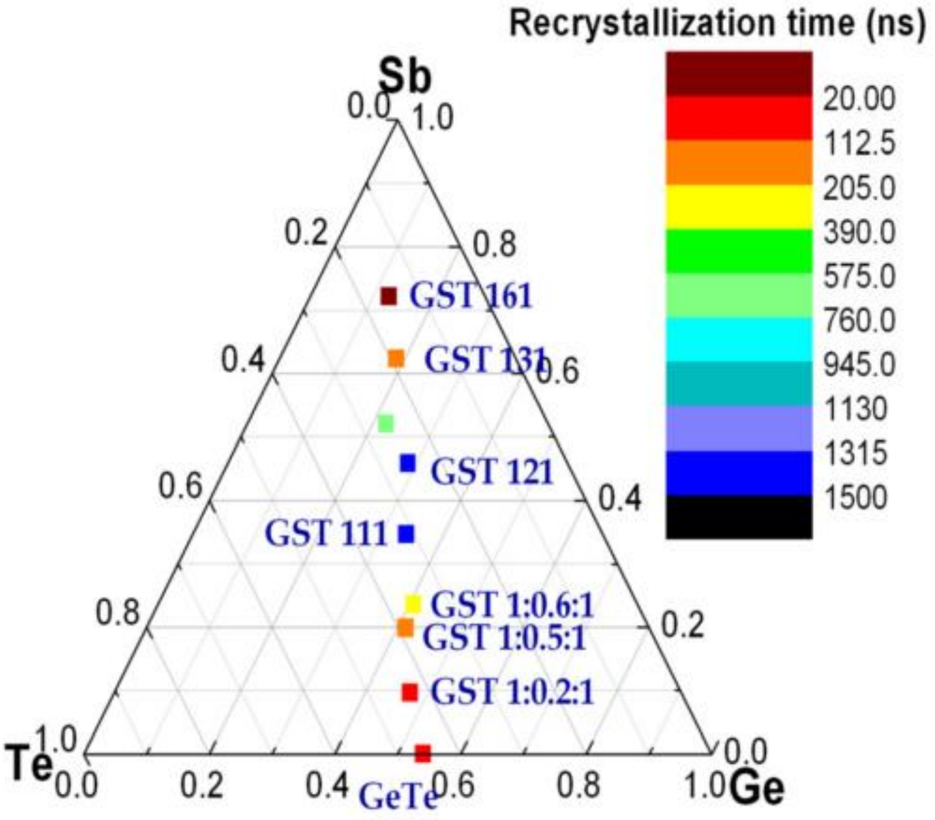
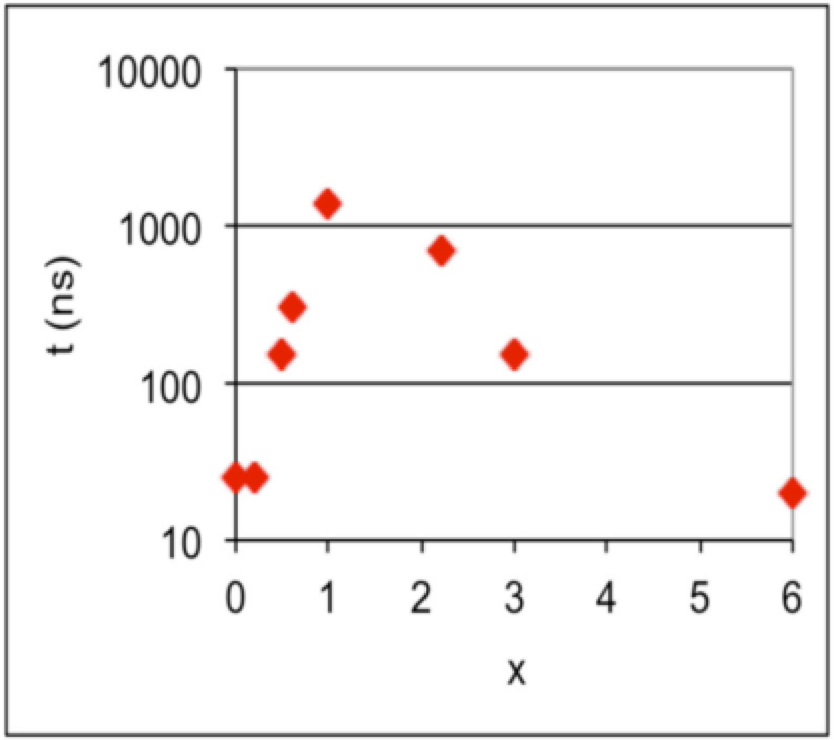
Crystallization properties of materials along the pseudo-binary line between GeTe and Sb

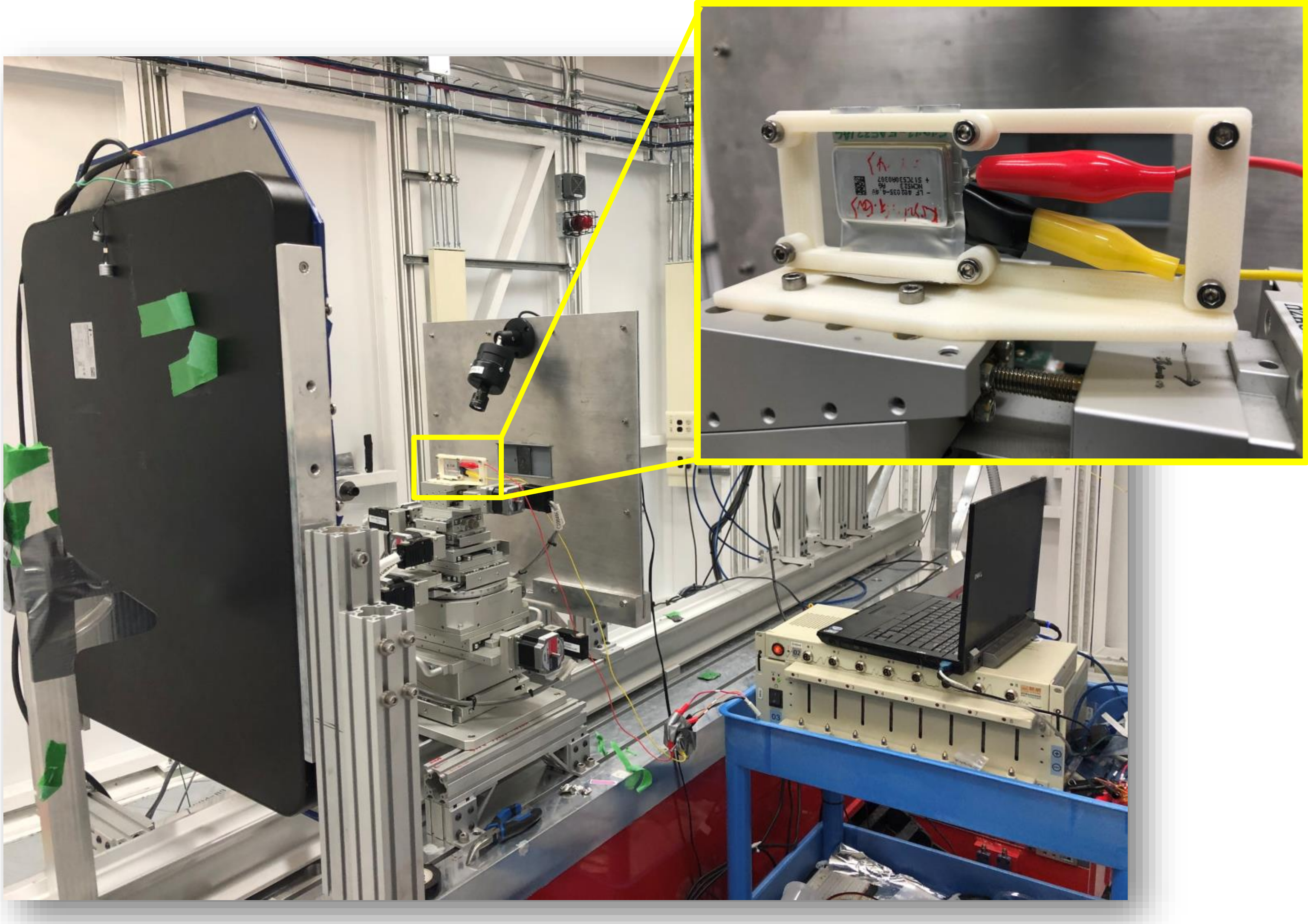




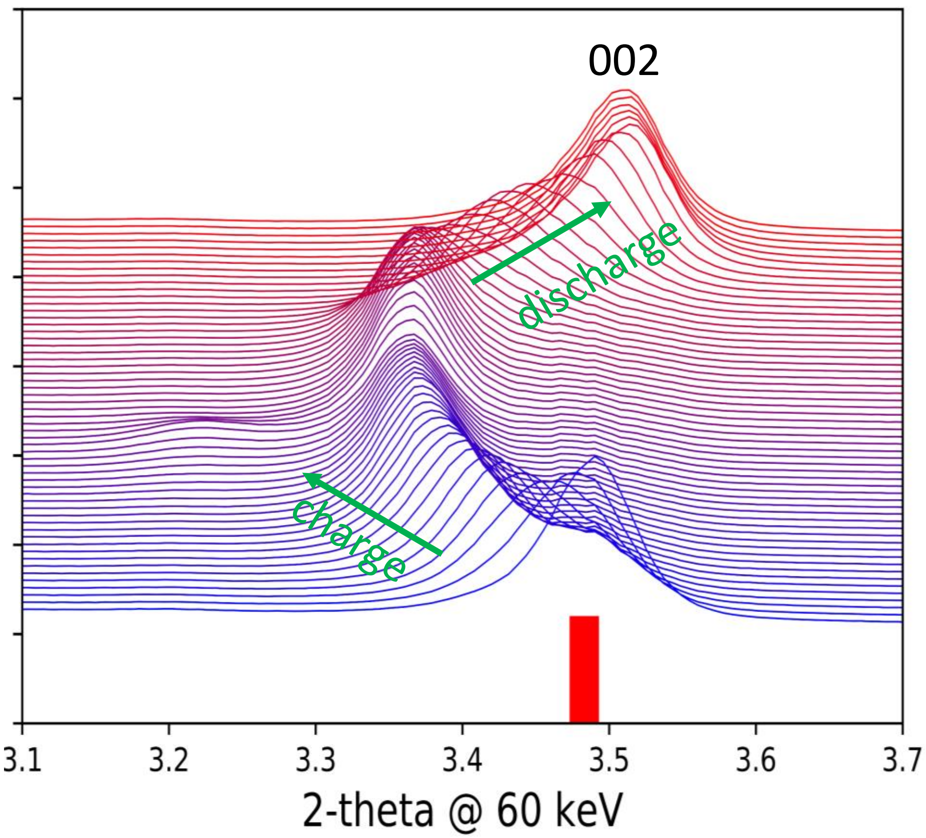
Journal of Applied Physics **115**, 093101 (2014)
Huai-Yu Cheng et al.

Battery experiments

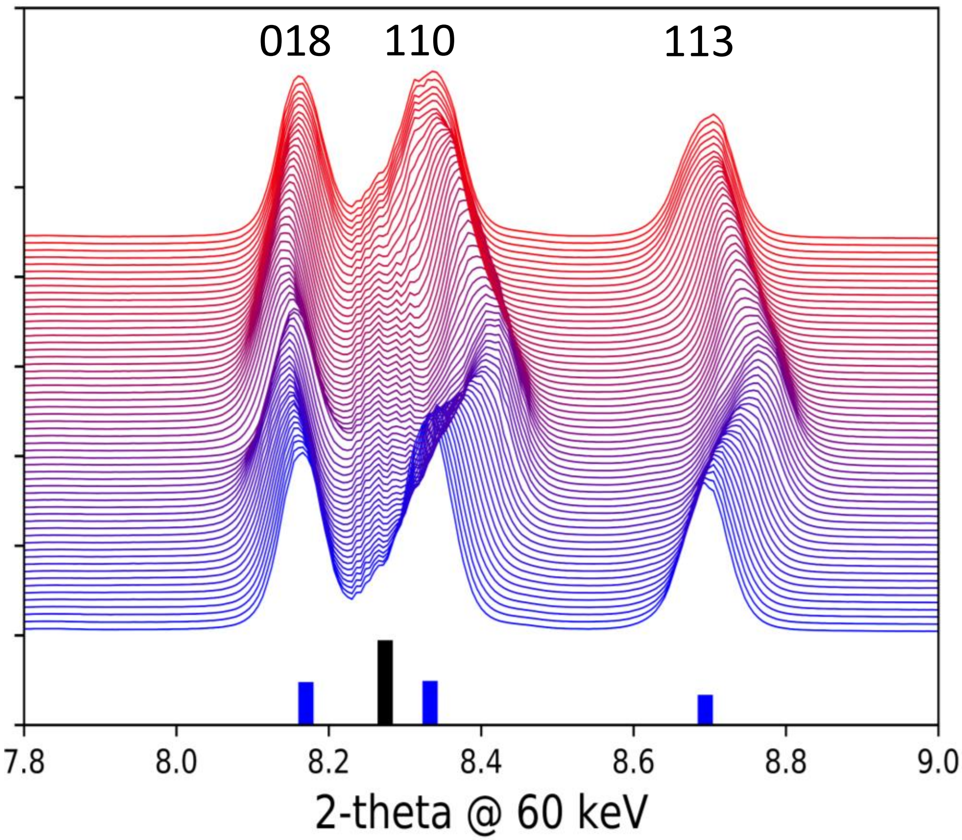
In-situ battery research



In-situ battery research



Anode (Graphite)



Cathode (Transition Metal Oxide)

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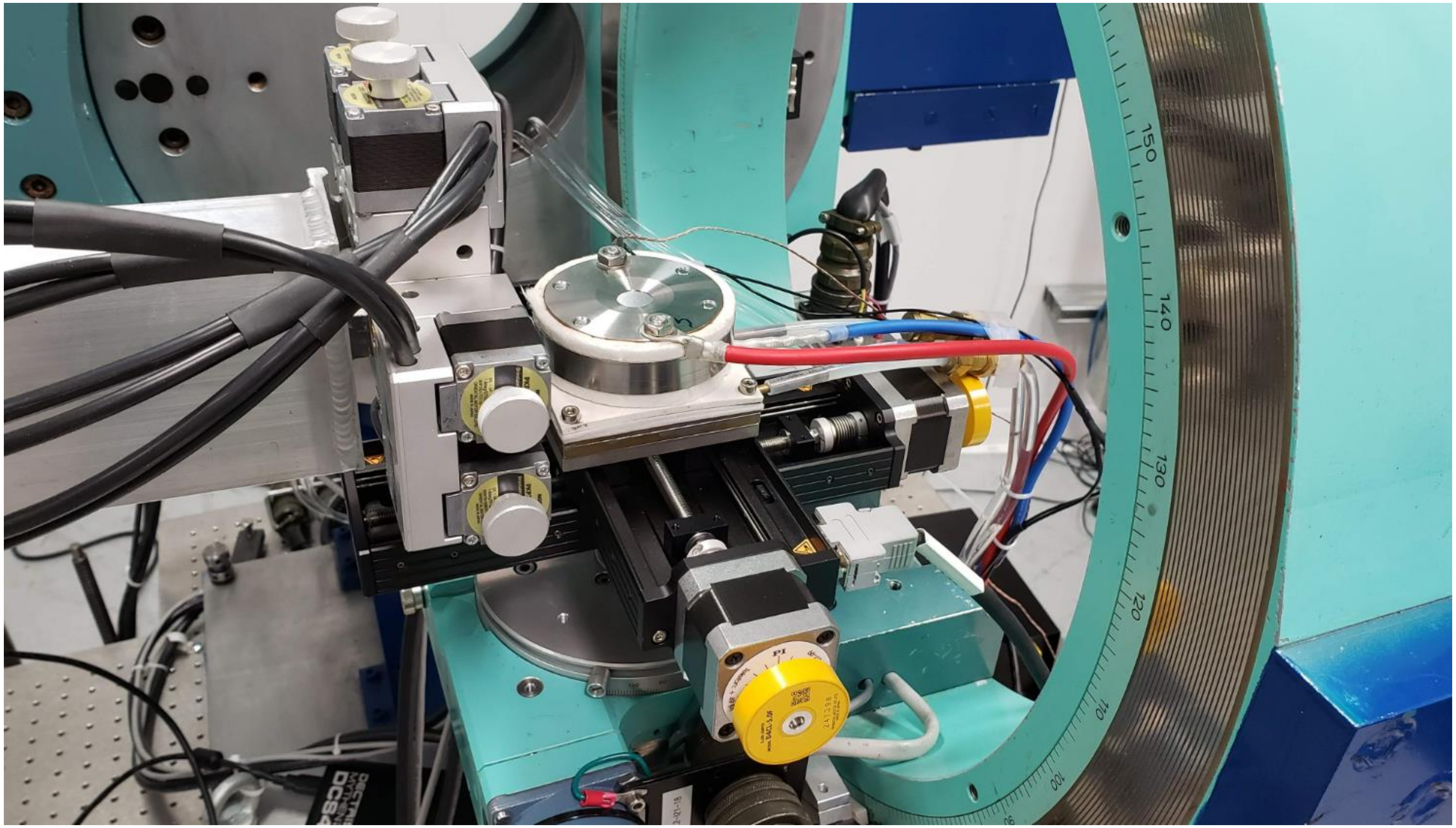
In-situ battery research

High Temperature Compatible Conflat Cell with Adjustable Stack Pressure for In-Situ and Operando X-Ray Studies of Lithium-Ion Battery Materials



Michael Fleischauer - NRC / University of Alberta

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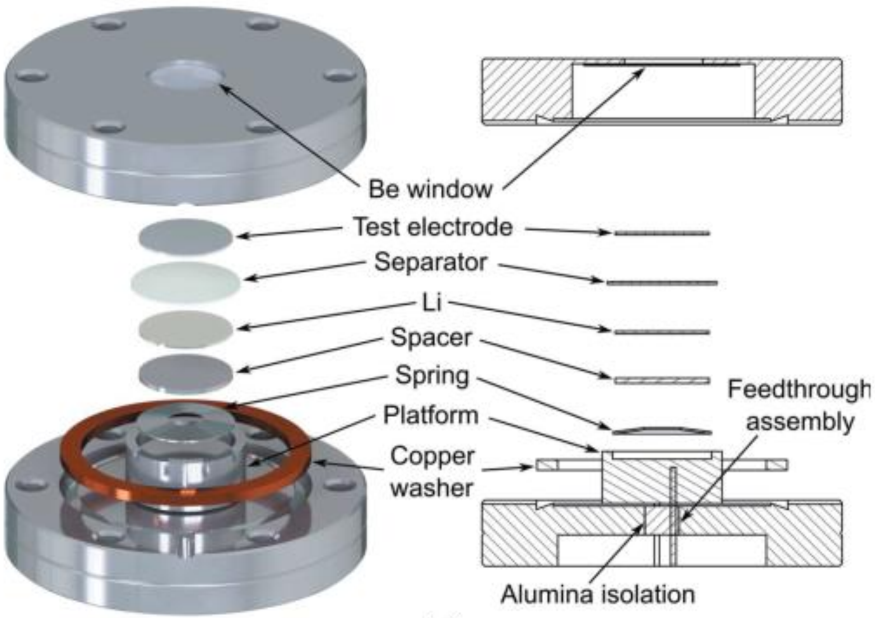
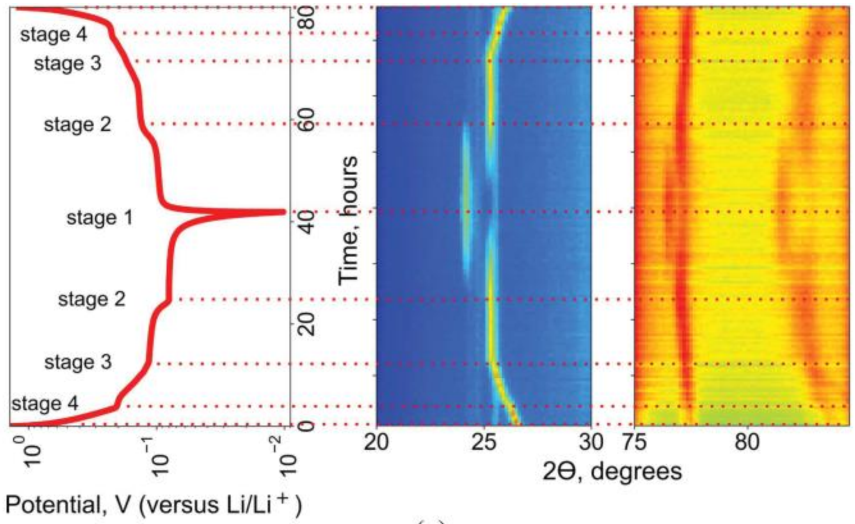
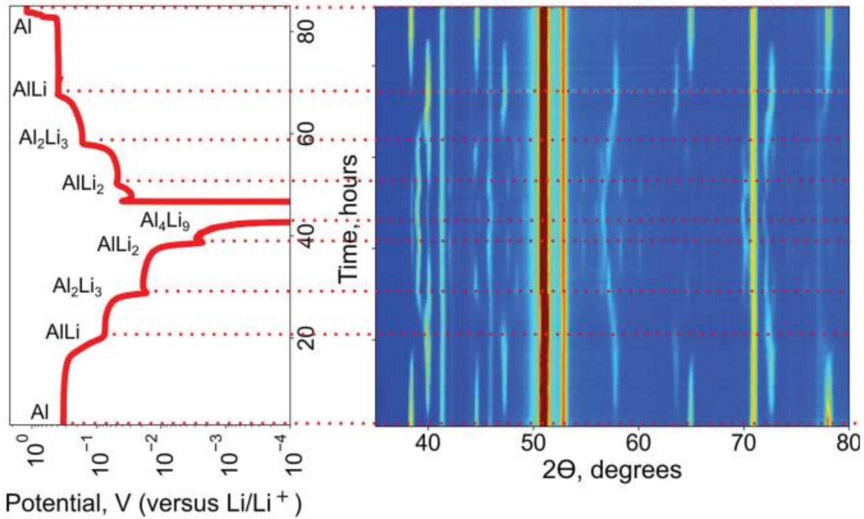
In-situ battery research



(*a*)

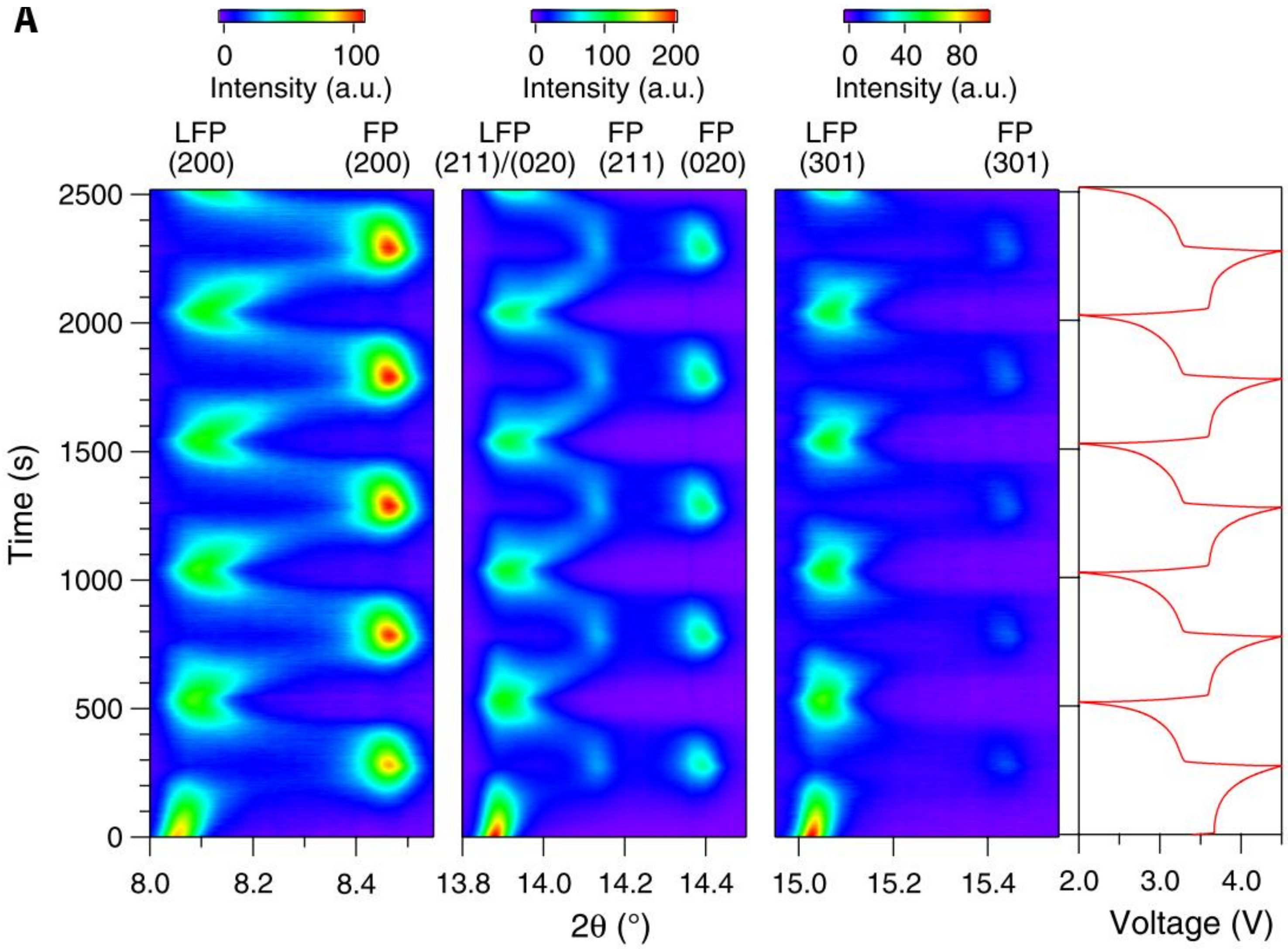


(*a*)



J. Appl. Cryst. (2021). **54**, 1416–1423

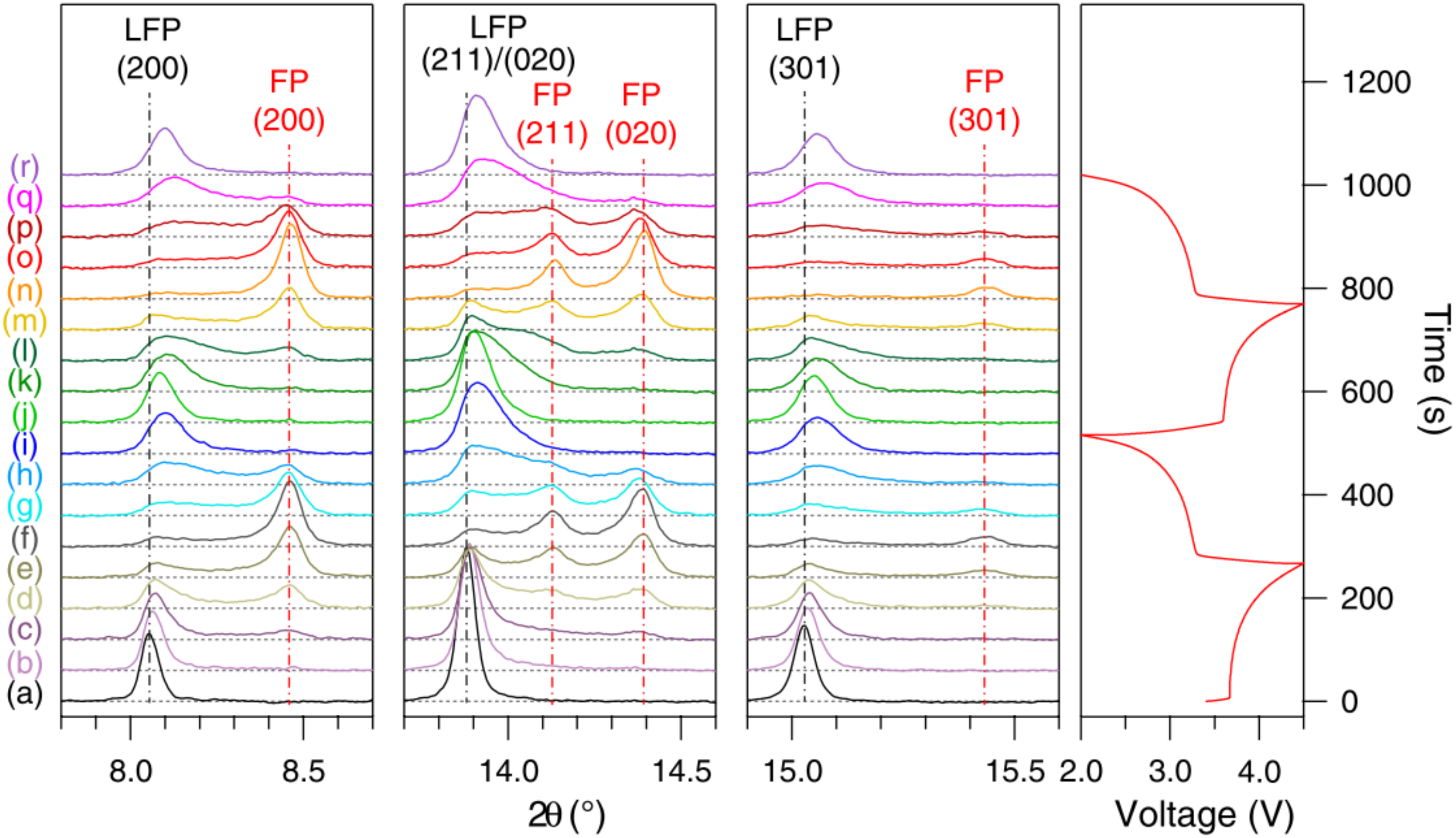
Capturing metastable structures during high-rate cycling of $LiFePO_4$ nanoparticle electrodes



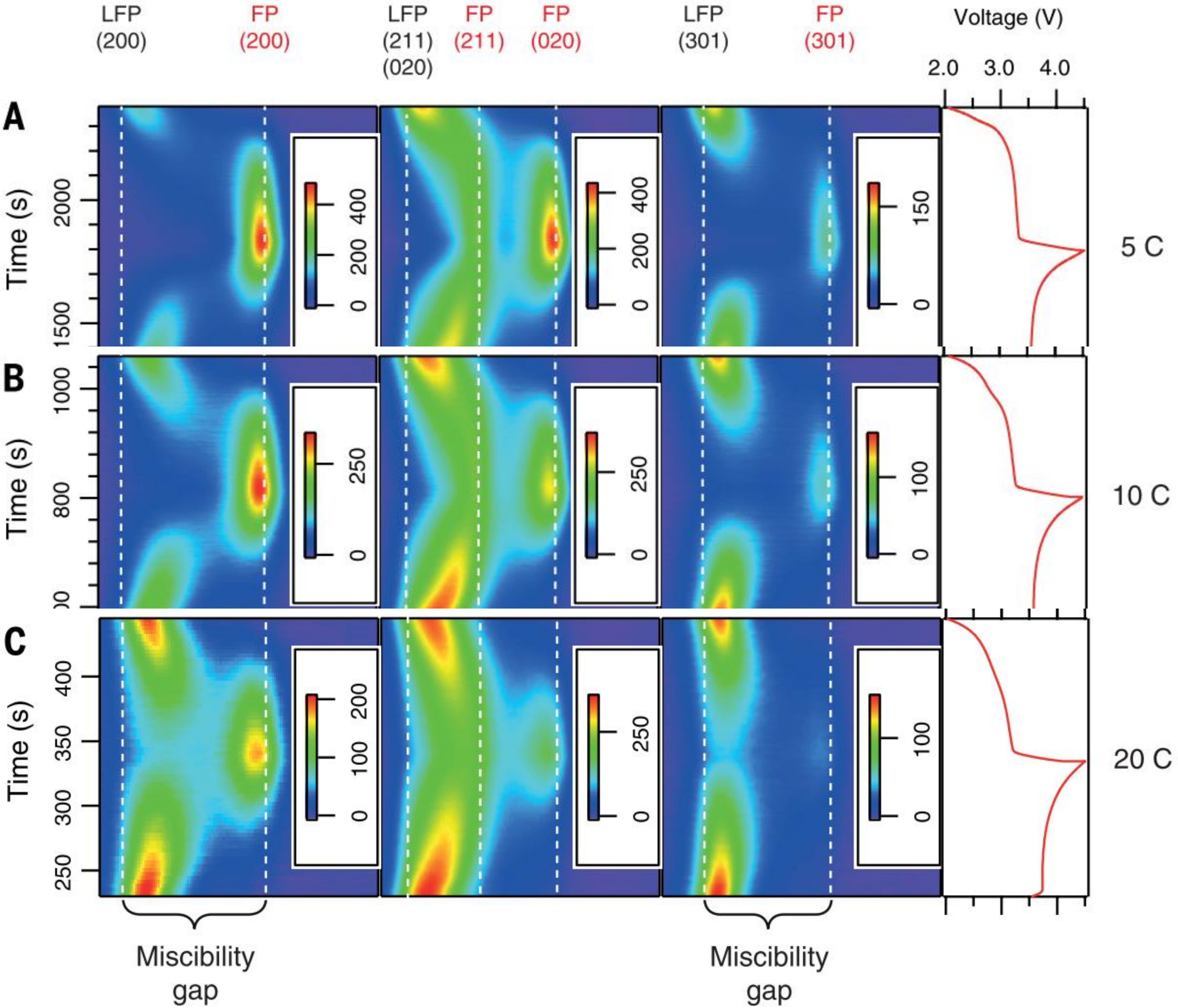
Liu et al. Science **344**(6191): 1252817

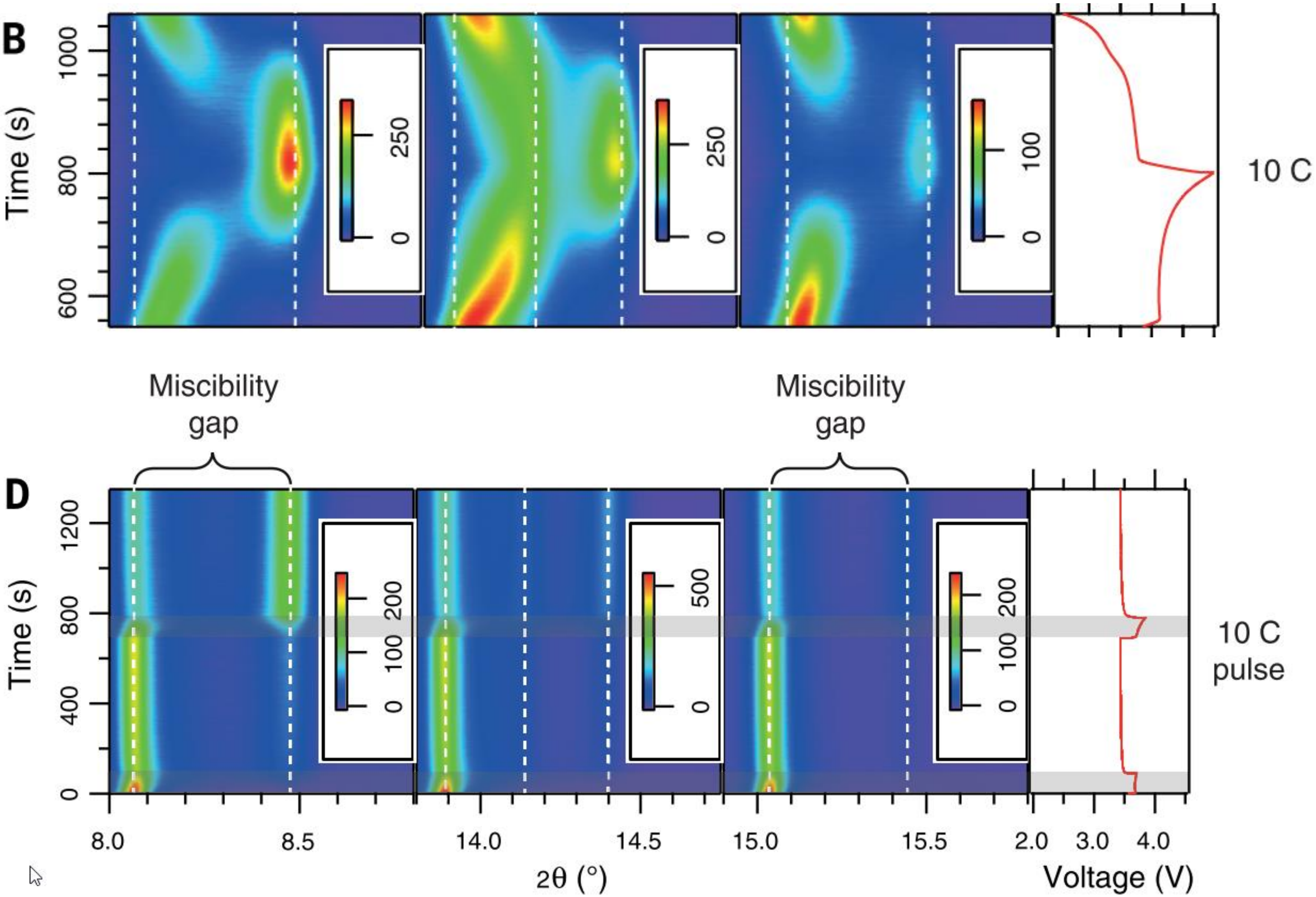
Capturing metastable structures during high-rate cycling of $LiFePO_4$ nanoparticle electrodes

B



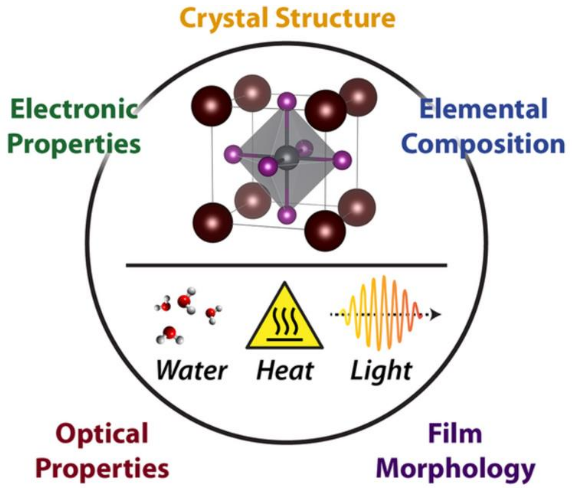
Liu et al. Science **344**(6191): 1252817

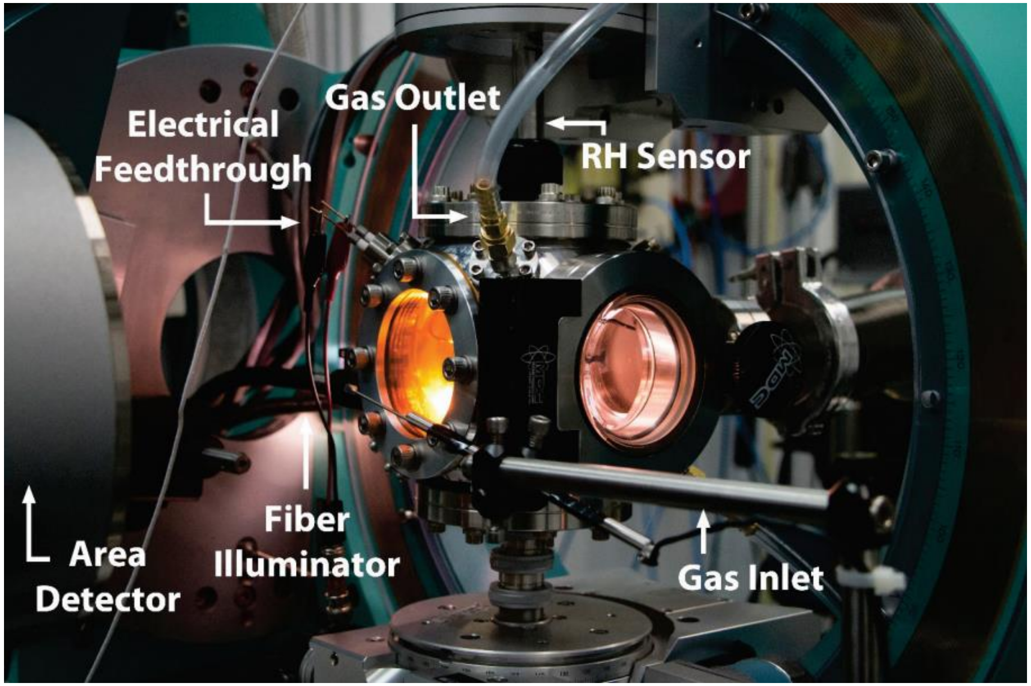

LFP (200)
FP (200)
LFP (211) (020)
FP (211)
FP (020)
LFP (301)
FP (301)
Voltage (V)
2.0
3.0
4.0
A
Time (s)
2000
1500
0
200
400
0
200
400
0
150
5 C
B
Time (s)
1000
800
0
250
0
250
0
100
10 C
C
Time (s)
400
350
300
250
0
100
200
0
250
0
100
20 C
Miscibility gap
Miscibility gap


B
Time (s)
600
800
1000
250
0
250
0
100
0
10 C
Miscibility gap
Miscibility gap
D
Time (s)
0
400
800
1200
200
100
0
500
0
200
100
0
10 C pulse
8.0
8.5
14.0
14.5
15.0
15.5
2θ (°)
2.0
3.0
4.0
Voltage (V)

Solar cell research

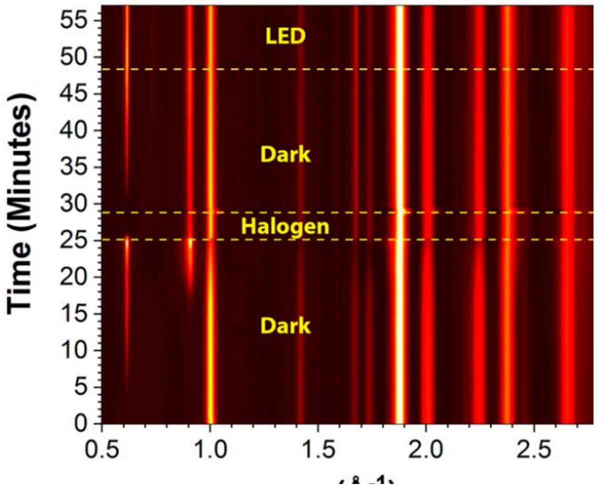
In situ studies of the degradation mechanisms of perovskite solar cells





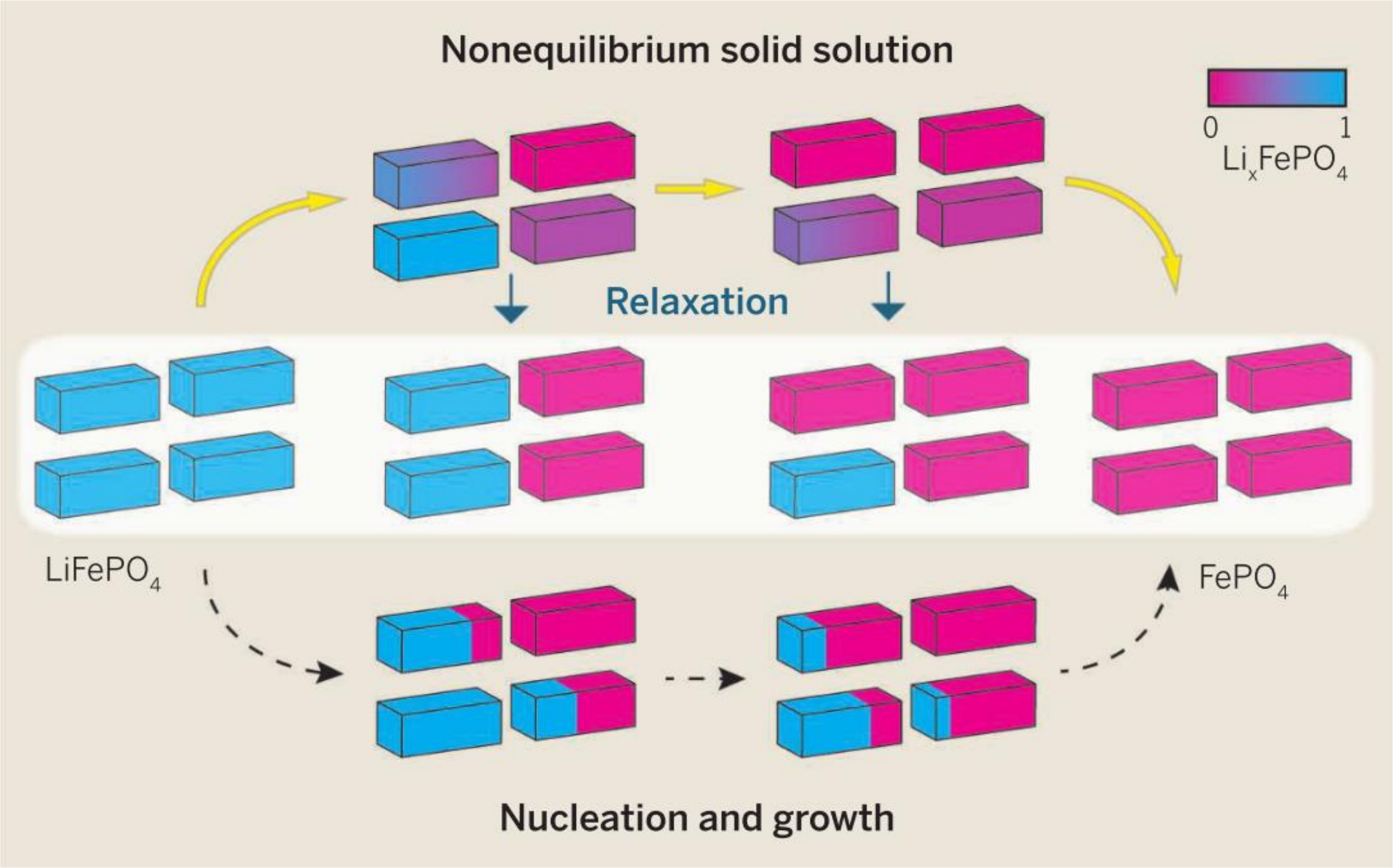
Elucidating the Failure Mechanisms of Perovskite Solar Cells in Humid Environments Using In Situ GI-WAXS

Tim Kelly - USASK



GIWAXS pattern of an ITO/ZnO/$CH_3NH_3PbI_3$/P3HT/Ag device exposed to a nitrogen atmosphere with RH ≈ 90%.

Capturing metastable structures during high-rate cycling of $LiFePO_4$ nanoparticle electrodes



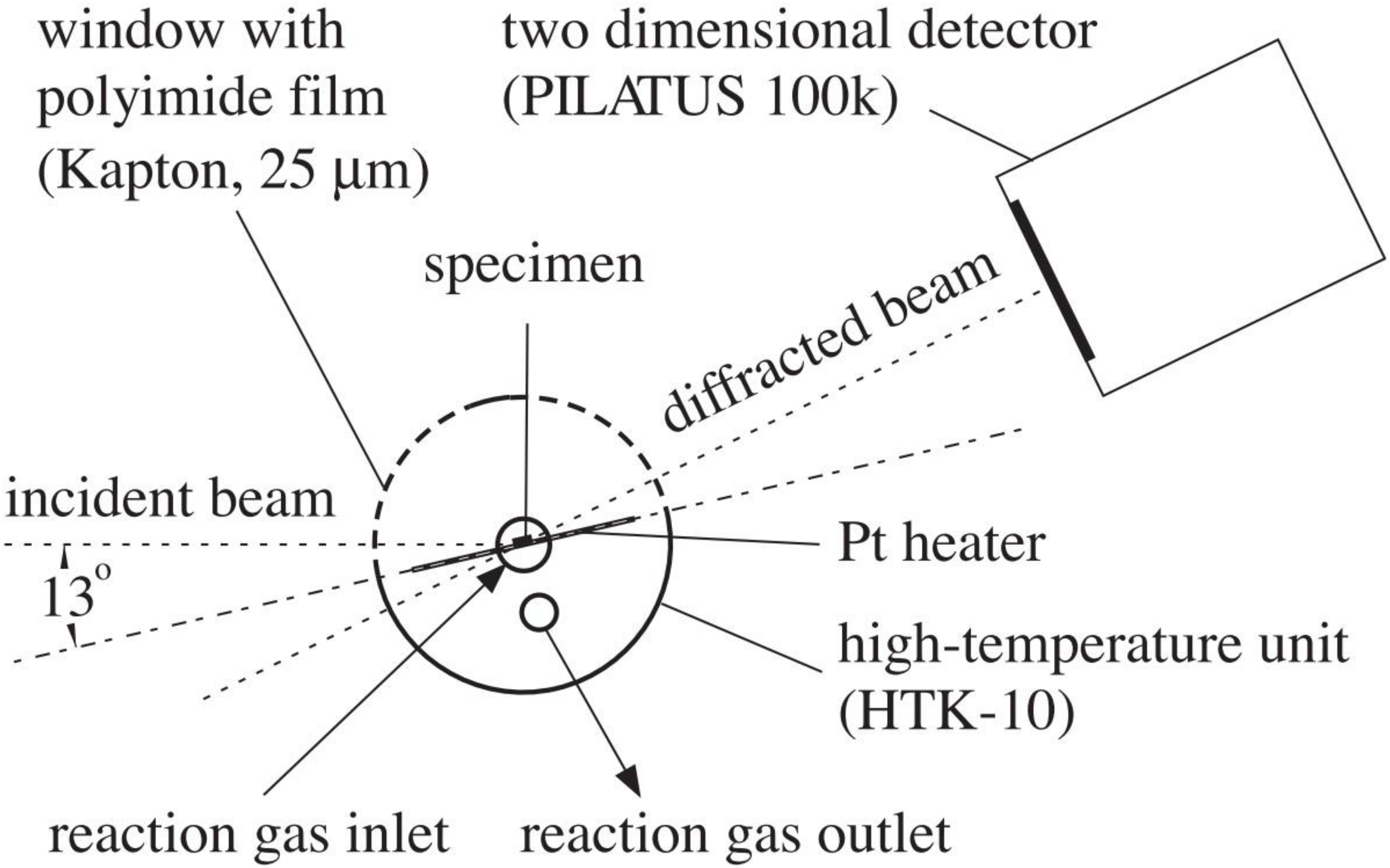
Liu et al. Science **344**(6191): 1252817

Corrosion studies

Corrosion can lead to failure involving personal injuries, fatalities, unscheduled shutdowns and environmental contamination

- One 2003 study estimated that the total annual direct and indirect **impact of corrosion** on the Canadian economy had a staggering $46.4 billion price tag.
- That’s roughly 2.5 % of Canada’s gross domestic product.

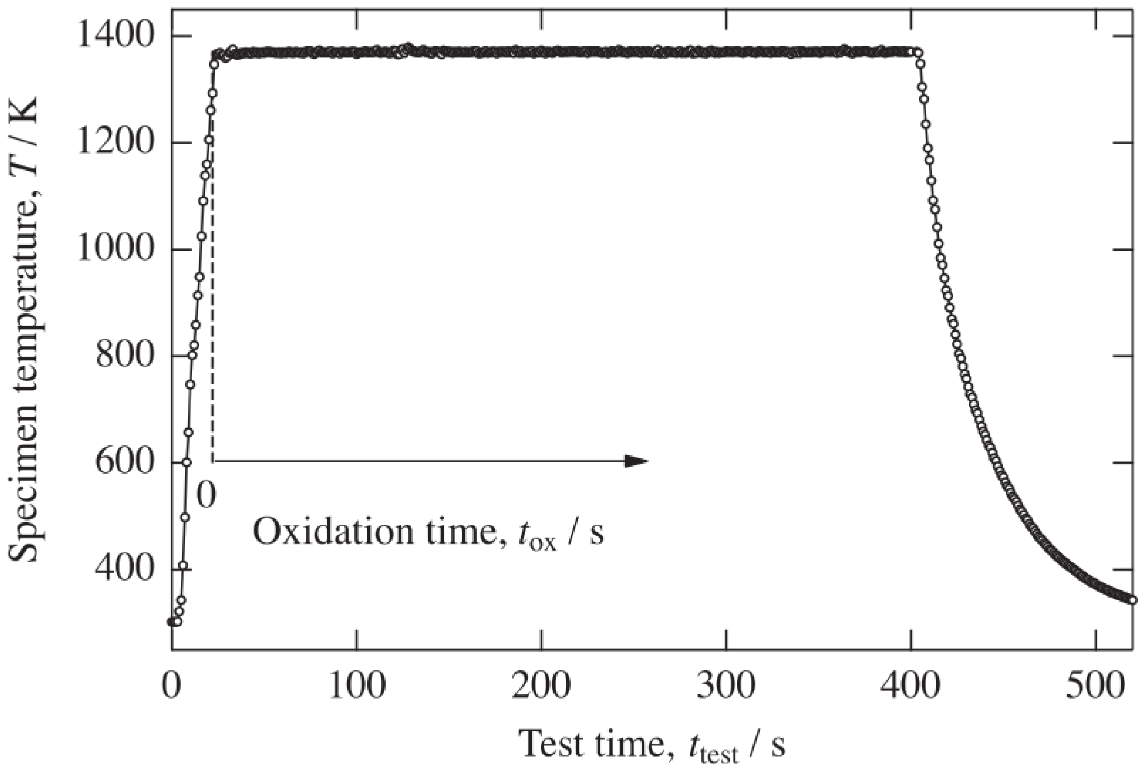
In situ studies of breakaway oxidation in type 430 stainless steel



BL-46XU in SPring-8

Saeki et al. Corrosion Science ***55****, 219, 2012*

In situ studies of breakaway oxidation in type 430 stainless steel



These specimens were heated at a rate of 50 K/s and
kept at 1373 K for ~400 s;

They were then cooled in the high-temperature unit.

Gas mixture:

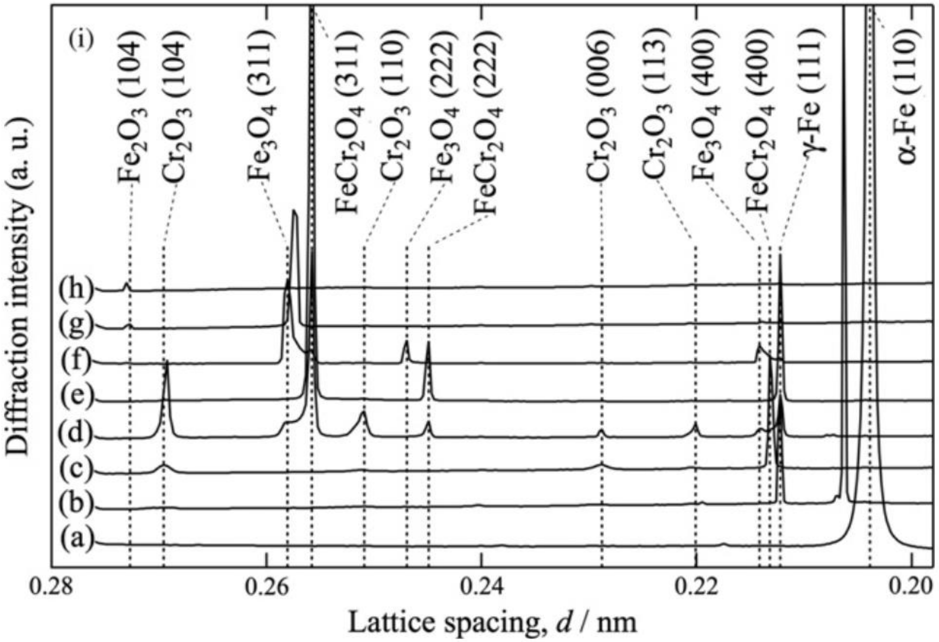
- 17 vol.% O2
- 20 vol.% H2O
- N2 gas

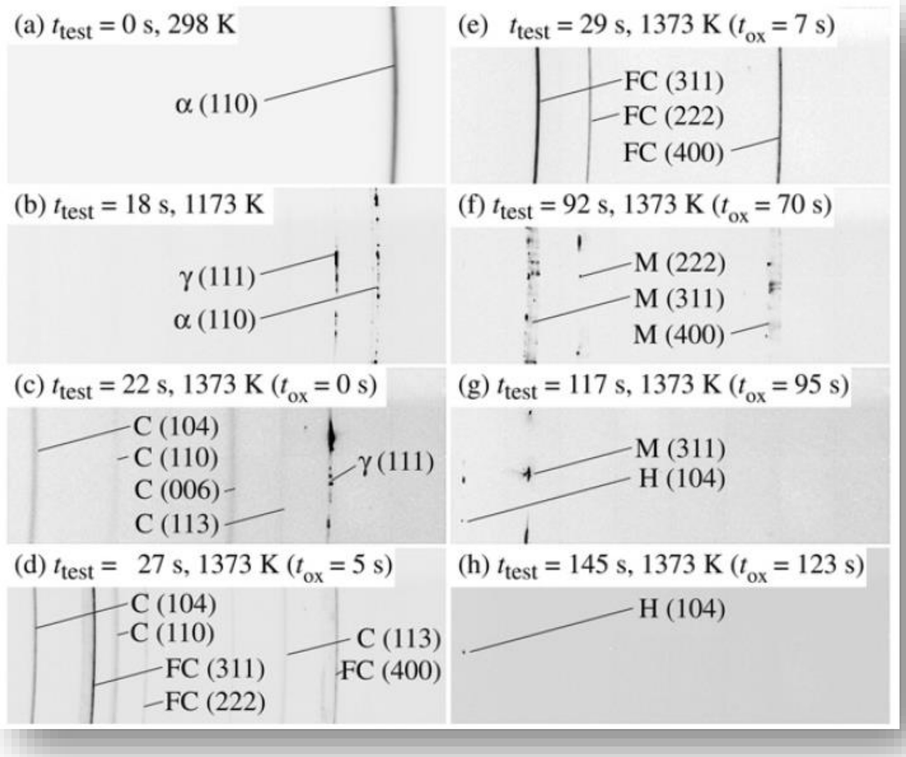
Rate of 8.3 cm^3/s

In situ studies of breakaway oxidation in type 430 stainless steel

Commercial type 430 stainless steel was used.
The composition of the steel was:

- 0.054 mass% C,
- 0.55 mass% Si,
- 0.09 mass% Mn,
- 0.004 mass% S,
- 0.13 mass% Ni,
- 16.1 mass% Cr,
- and Fe





*Saeki et al. Corrosion Science **55**, 219, 2012*

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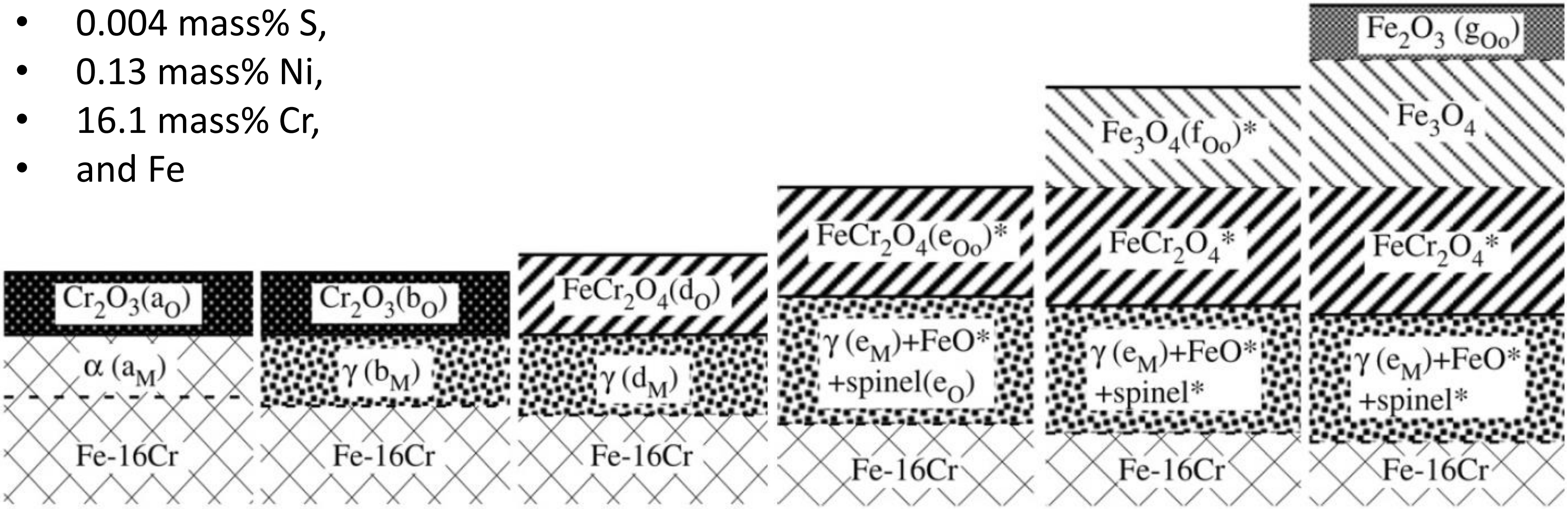


Saeki et al. Corrosion Science ***55****, 219, 2012*

In situ mechanical testing

Gleeble 3S50

Gleeble®Synchrotron

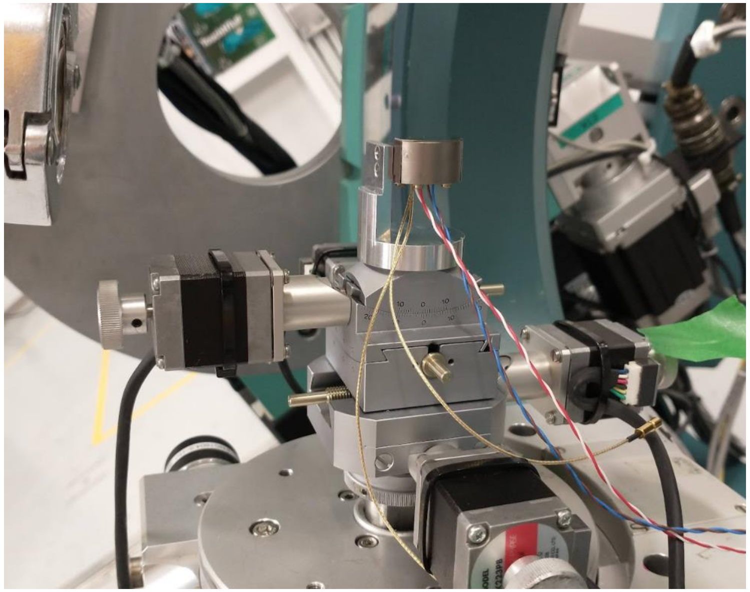
Allows the material of interest to be subject to a wide range of thermo-mechanical conditions

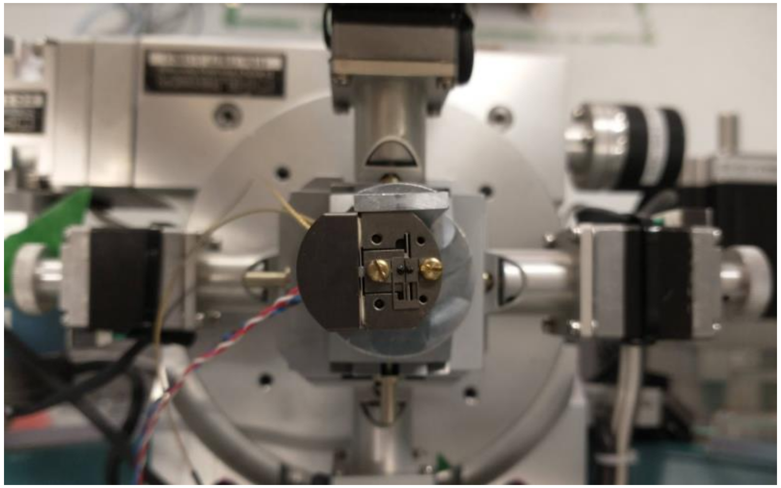
Applications:

- ✓ Phase transformations
- ✓ Residual stress evolution
- ✓ Corrosion
- ✓ Oxidation

https://www.gleeble.com/products/specialty-systems/gleeble-synchrotron.html

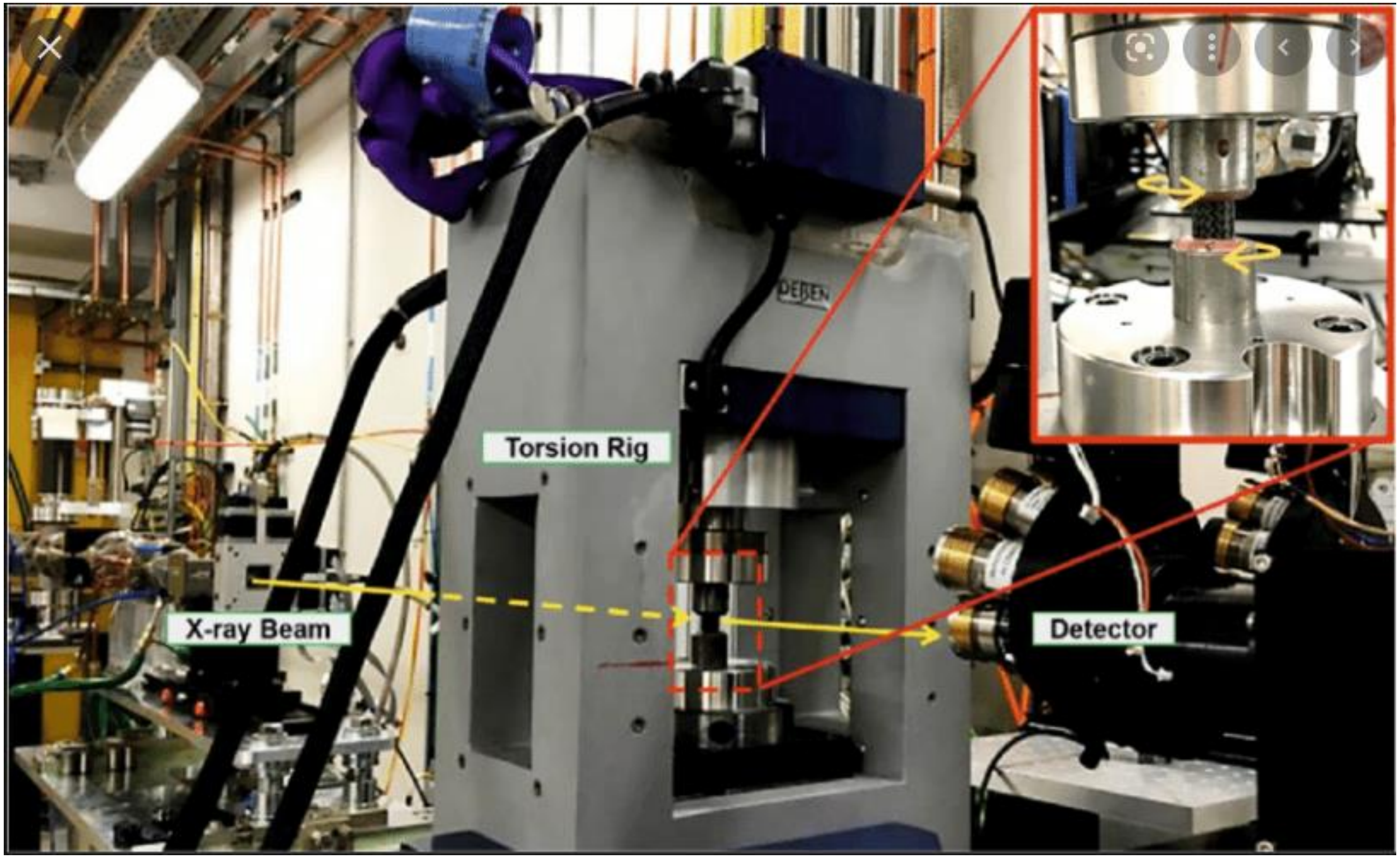
Razorbill strain cell



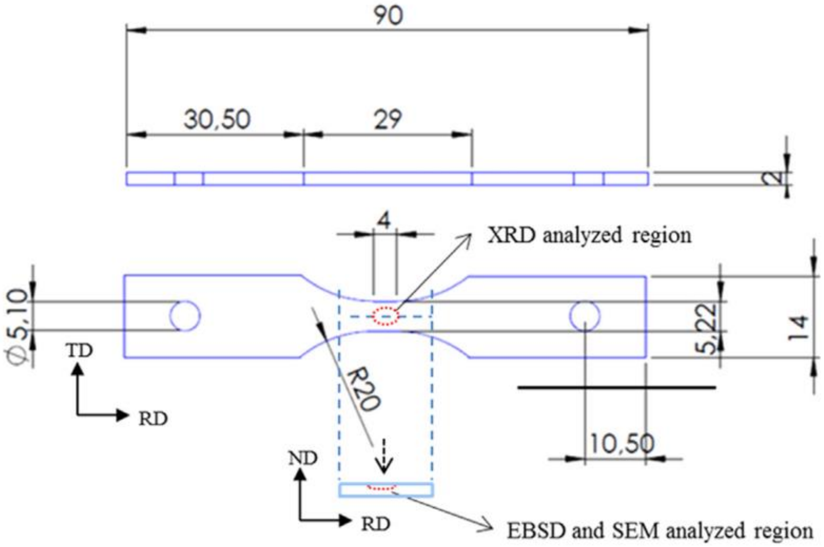


https://razorbillinstruments.com/uniaxial-strain-cell/

Deben 20kN stress rig at Diamond

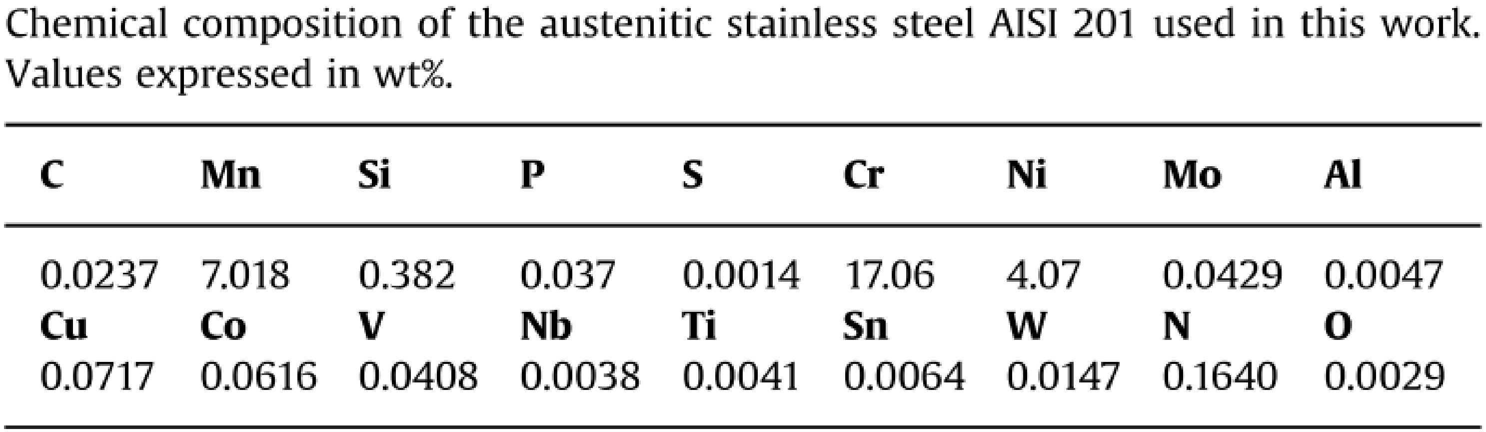


In-situ synchrotron x-ray evaluation of strain-induced martensite in AISI 201 austenitic stainless steel during tensile testing



<u>Goal:</u>

- To understand the changes in microstructure of AISI 201 by applying a tensile stress using in-situ XRD.
- To track phase transformation and strain partitioning among the phases

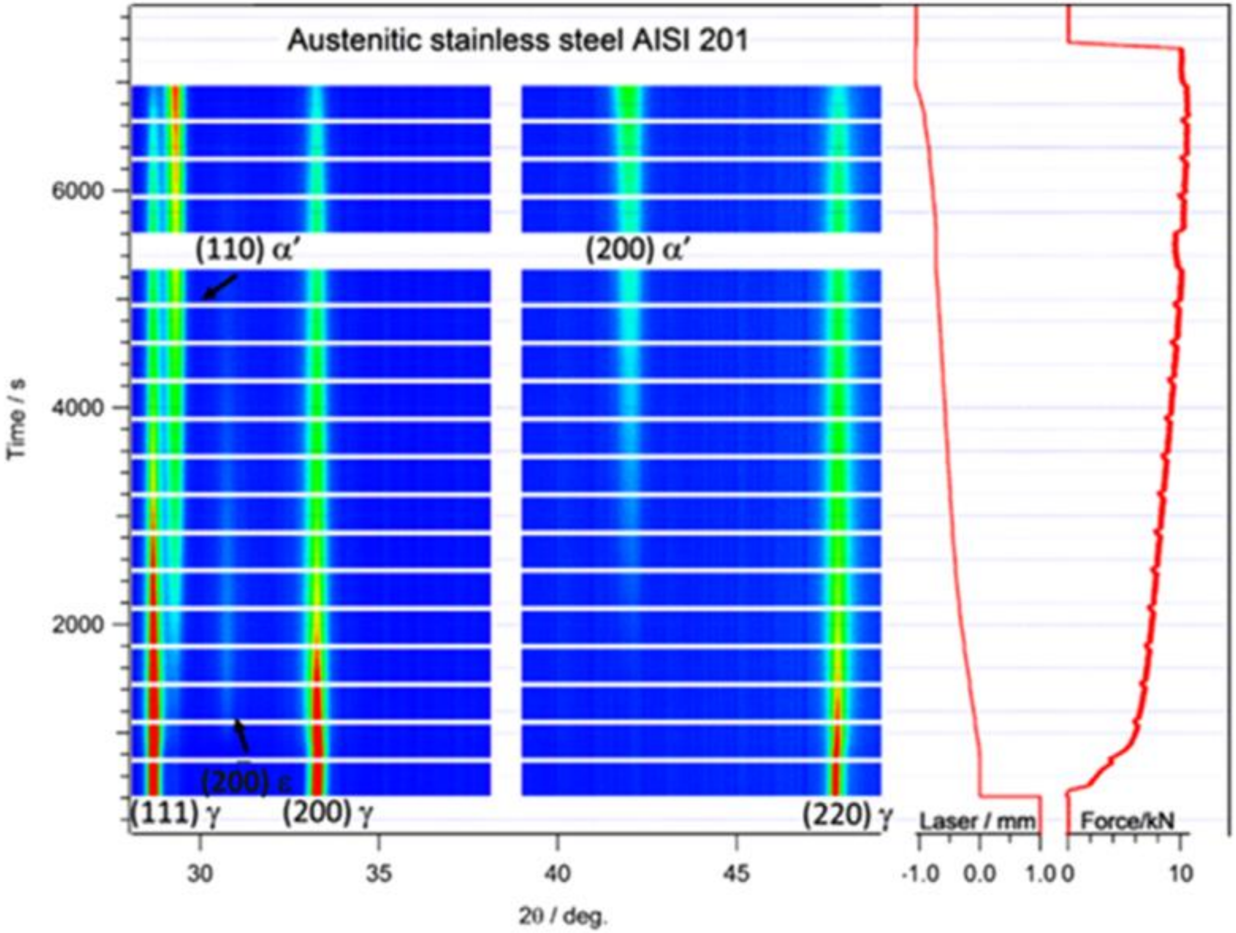


Chemical composition of the austenitic stainless steel AISI 201 used in this work. Values expressed in wt%.

C	**Mn**	**Si**	**P**	**S**	**Cr**	**Ni**	**Mo**	**Al**
0.0237	7.018	0.382	0.037	0.0014	17.06	4.07	0.0429	0.0047
Cu	**Co**	**V**	**Nb**	**Ti**	**Sn**	**W**	**N**	**O**
0.0717	0.0616	0.0408	0.0038	0.0041	0.0064	0.0147	0.1640	0.0029

Gauss, C. et al. Materials Science & Engineering A **651**, 507, 2016

In-situ synchrotron x-ray evaluation of strain-induced martensite in AISI 201 austenitic stainless steel during tensile testing

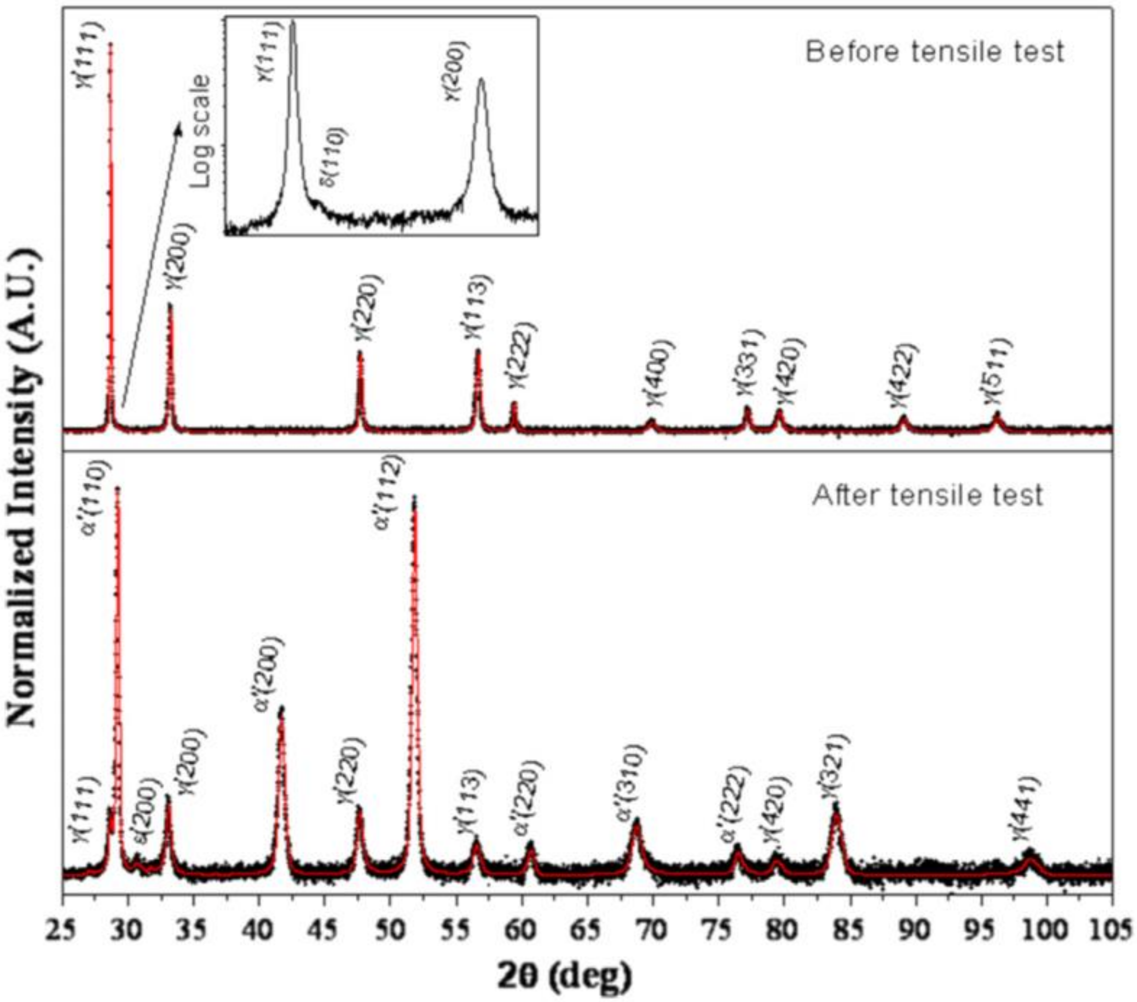


Metastable austenite (γ) decomposes into

- hcp-ε-martensite and
- bcc-α'-martensite

Gauss, C. et al. Materials Science & Engineering A **651**, 507, 2016

In-situ synchrotron x-ray evaluation of strain-induced martensite in AISI 201 austenitic stainless steel during tensile testing



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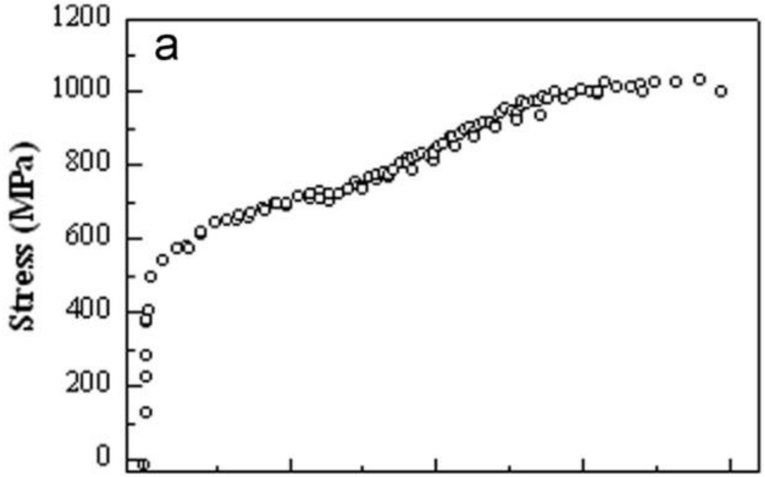
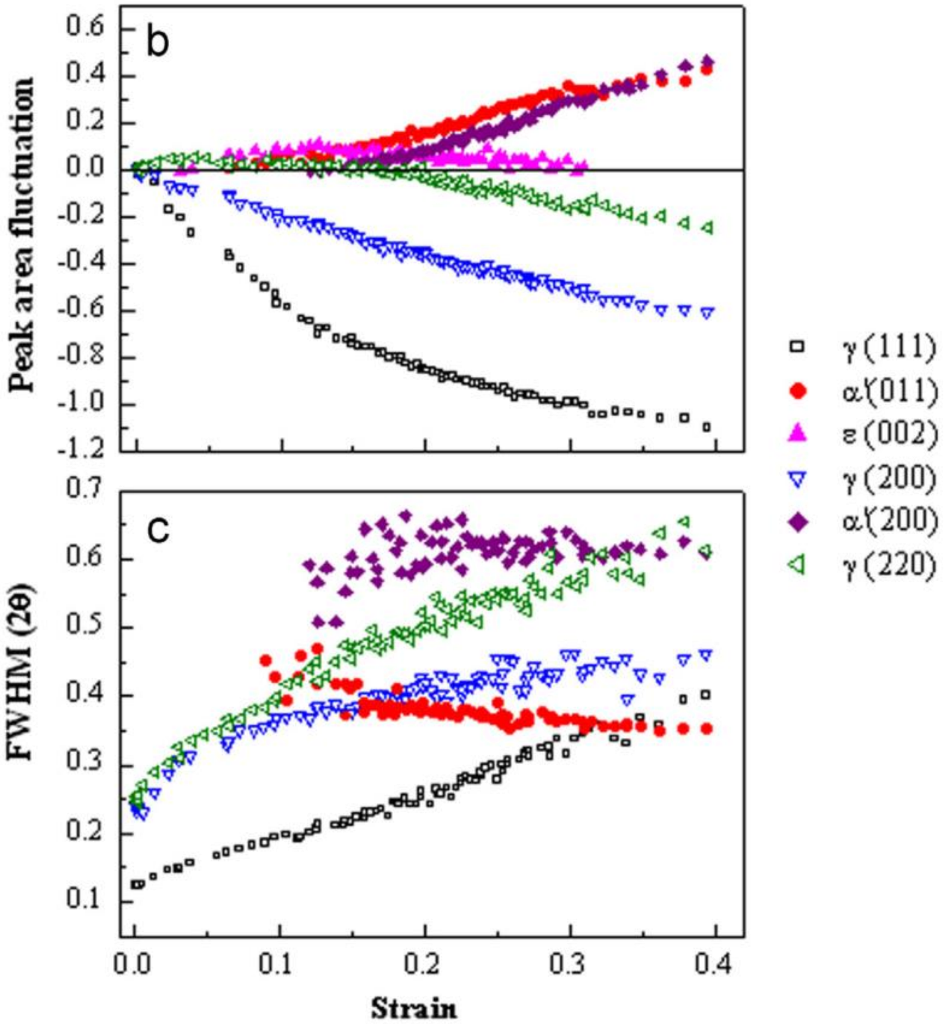
651, 507, 2016

In-situ synchrotron x-ray evaluation of strain-induced martensite in AISI 201 austenitic stainless steel during tensile testing



Data analysis:

- ✓ Phase identification
- ✓ Integrated intensity
- ✓ Peak position
- ✓ FWHM



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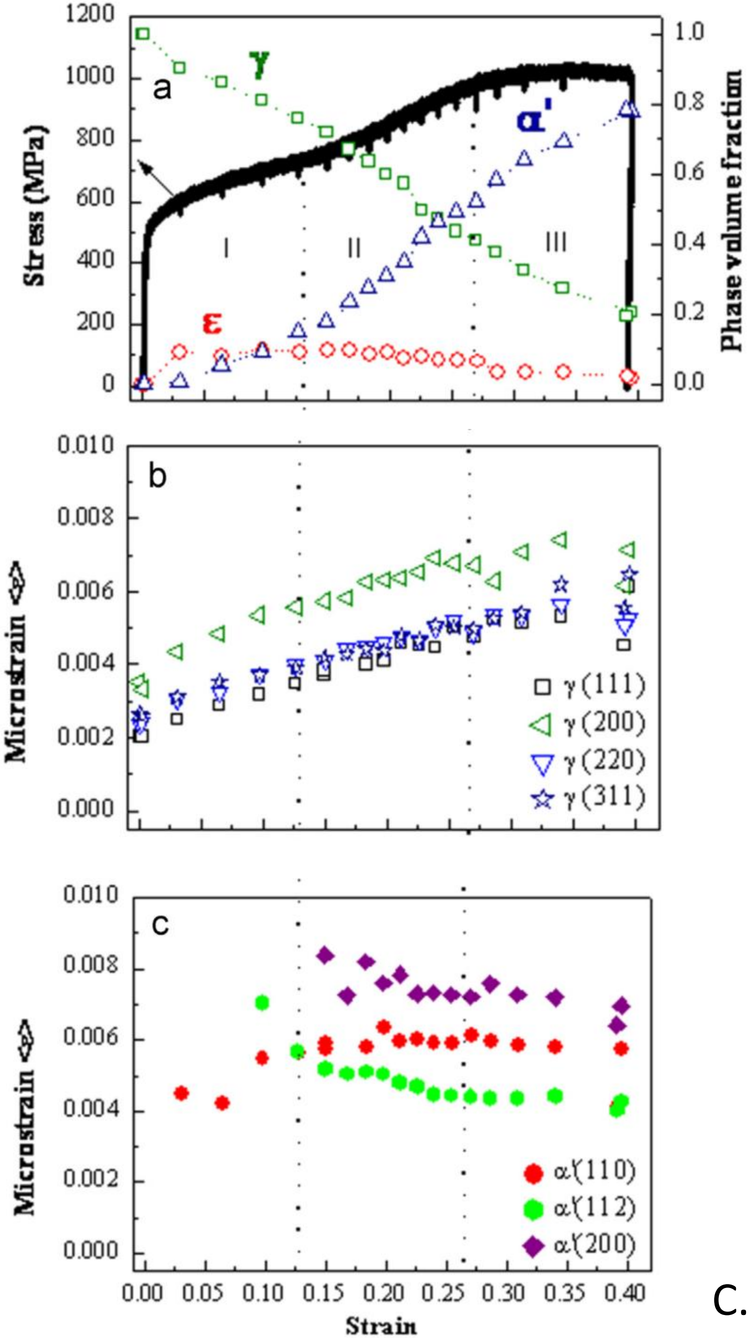
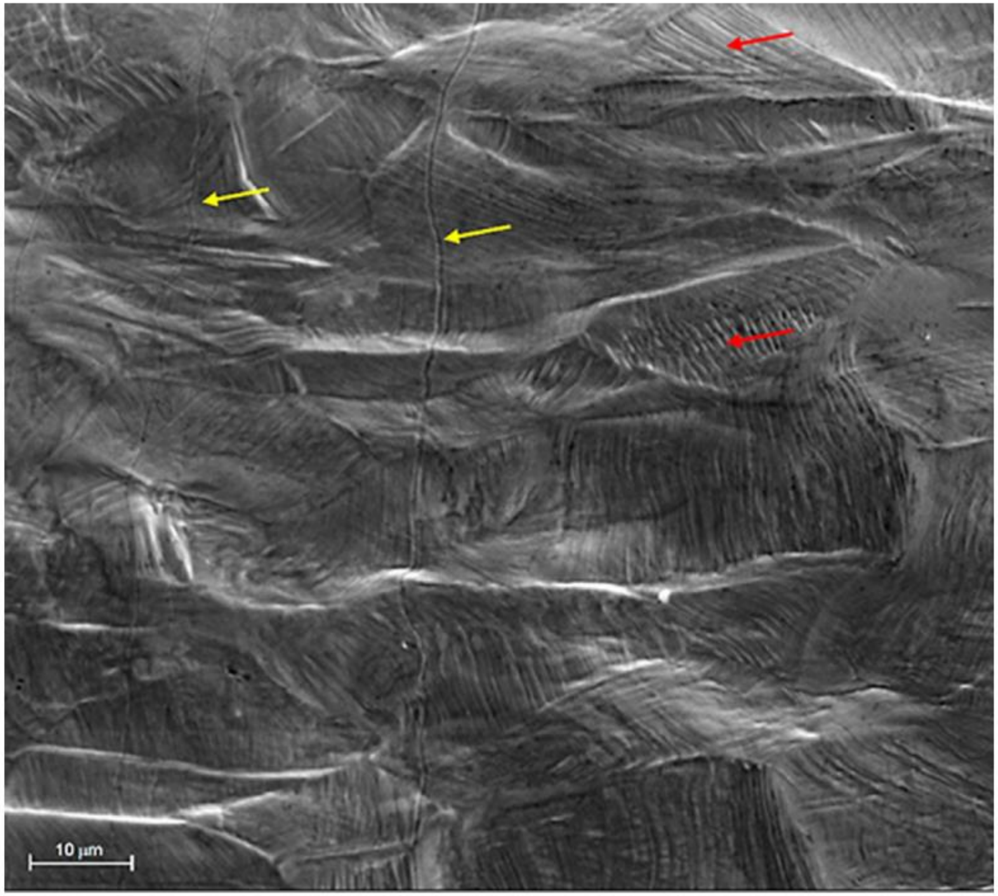
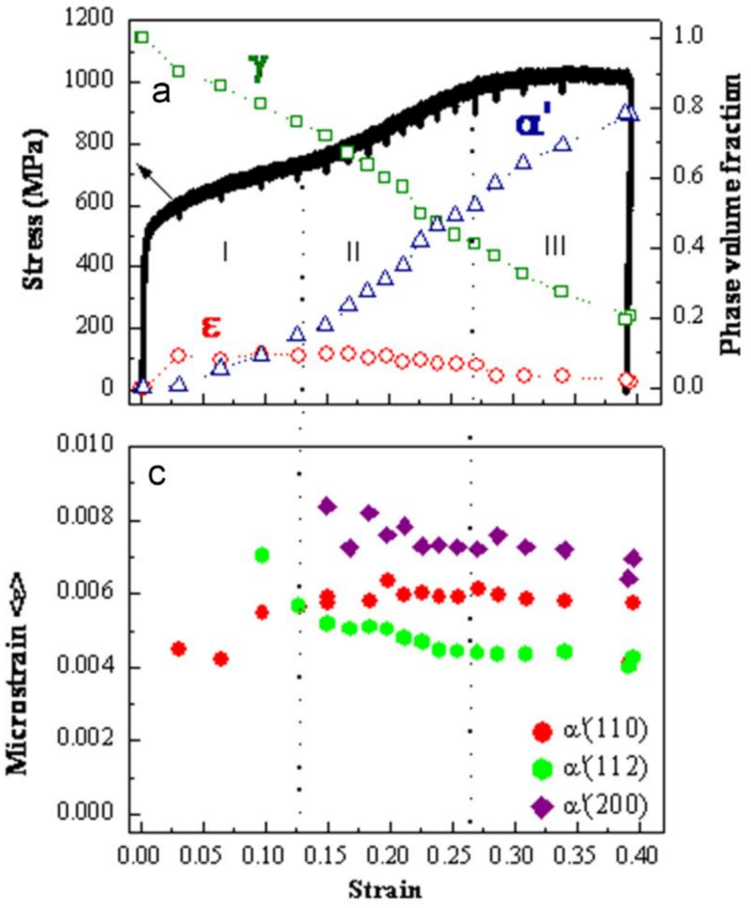
Gauss, C. et al. Materials Science & Engineering A **651**, 507, 2016





C. Gauss. Materials Science & Engineering A **651**, 507, 2016

In-situ synchrotron x-ray evaluation of strain-induced martensite in AISI 201 austenitic stainless steel during tensile testing



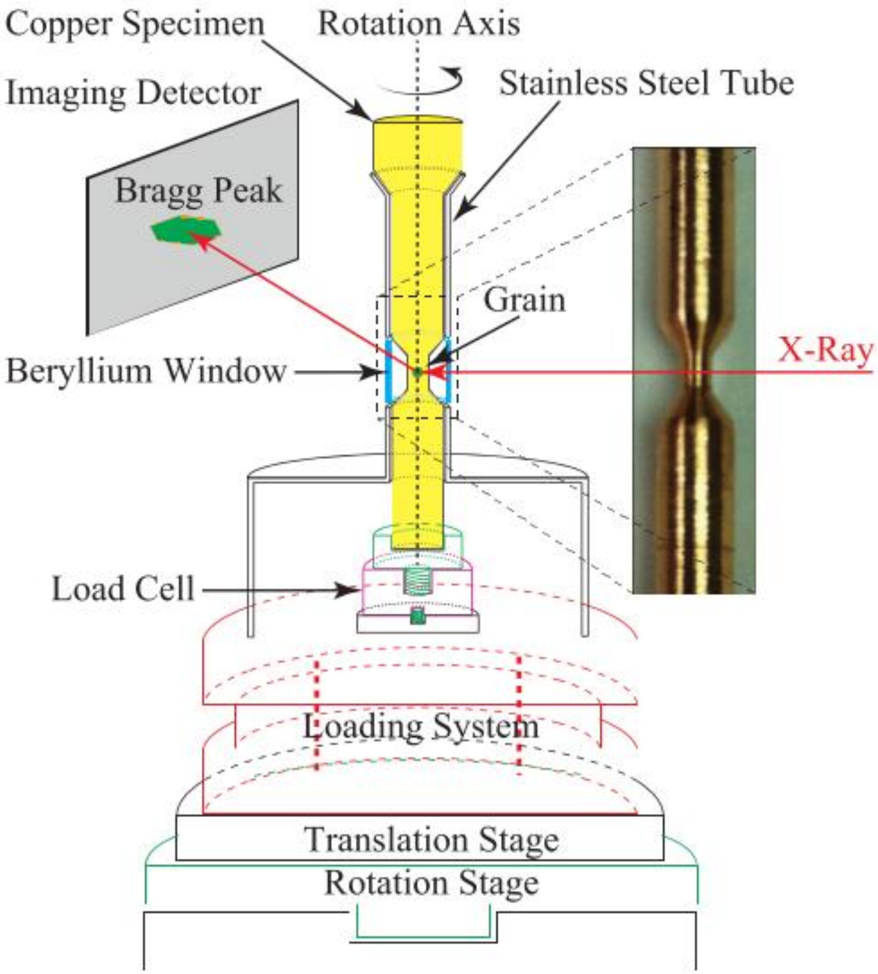
- ✓ The strain induced transformation of metastable gamma austenite(fcc structure) was followed in real time.
- ✓ ε-martensite is the first phase to appear followed by α' – martensite.
- ✓ Got information about the phase volume fractions and microstrain.
- ✓ FWHM of peaks is related to macroscopic mechanical properties. FWHM remains constant in the elastic regime and increases at the yield strength with the onset of plastic flow.

Gauss, C. et al. Materials Science & Engineering A **651**, 507, 2016

In-situ observation of bulk 3D grain evolution during plastic deformation in polycrystalline Cu

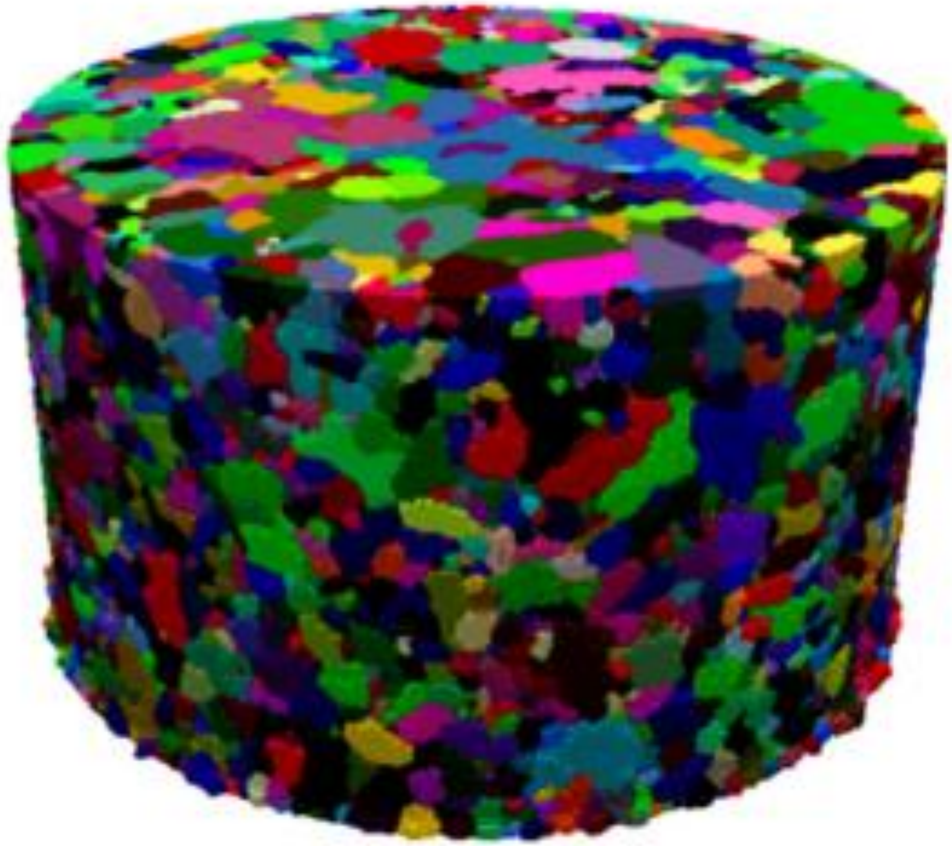
Reeju Pokharel [a,c,*], Jonathan Lind [a,b], Shiu Fai Li [b], Peter Kenesei [d], Ricardo A. Lebensohn [c], Robert M. Suter [a], Anthony D. Rollett [a]

99.995% pure polycrystalline copper during tensile loading



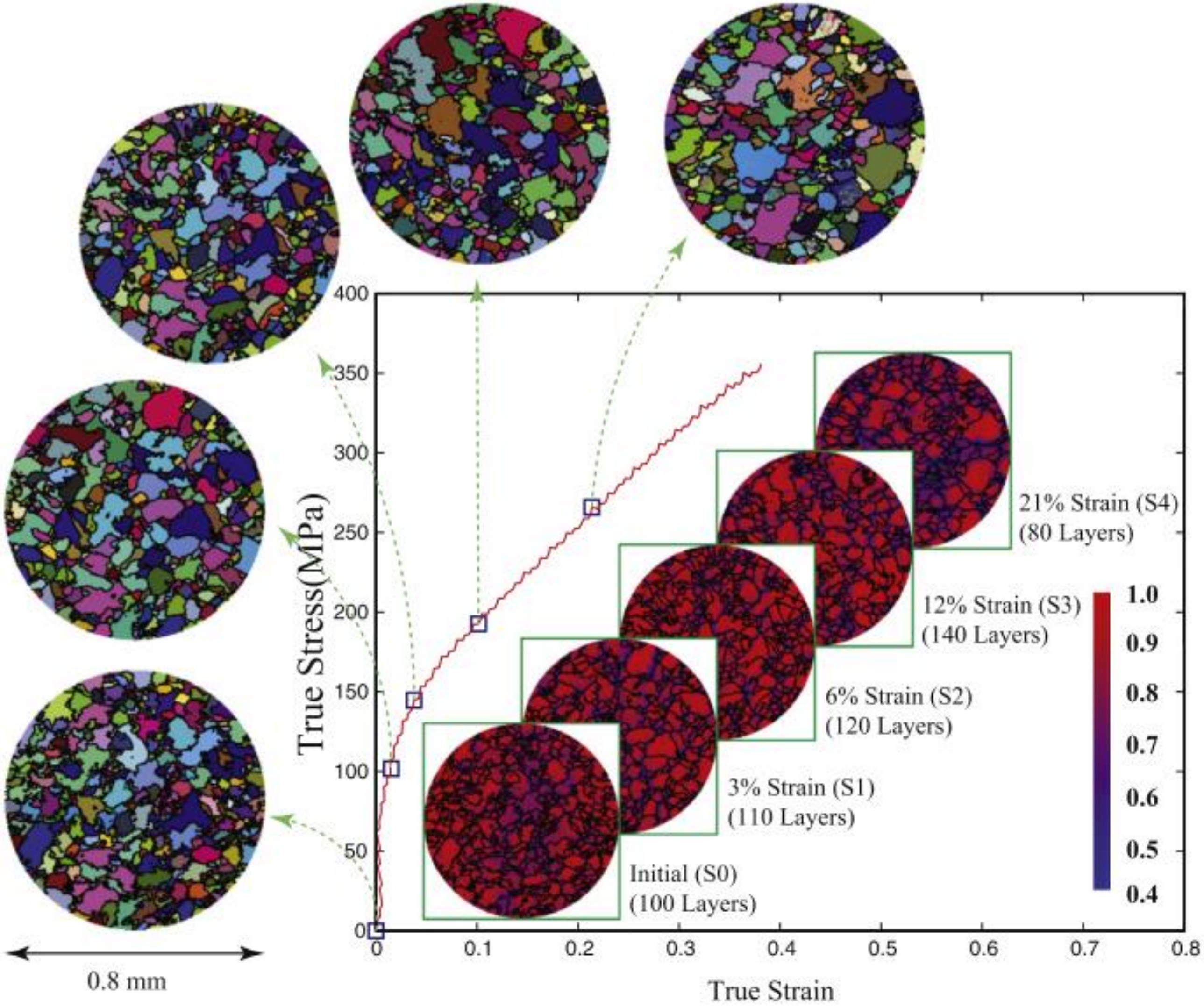
R. Pokharel et al. / International Journal of Plasticity 67 (2015) 217–234

In-situ observation of bulk 3D grain evolution during plastic deformation in polycrystalline Cu



99.995%pure polycrystalline copper during tensile loading

In-situ observation of bulk 3D grain evolution during plastic deformation in polycrystalline Cu



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R. Pokharel et al. / International Journal of Plasticity 67 (2015) 217–234

Catalysts

Oil refinery catalytic reactor

Catalysis

Catalysts play an important part in many chemical processes. More than 85% of chemicals come from catalytic reactions

Catalysts:

- increase the rate of reaction
- are not consumed by the reaction
- are only needed in very small amounts

In-situ and operando catalytic experiments include

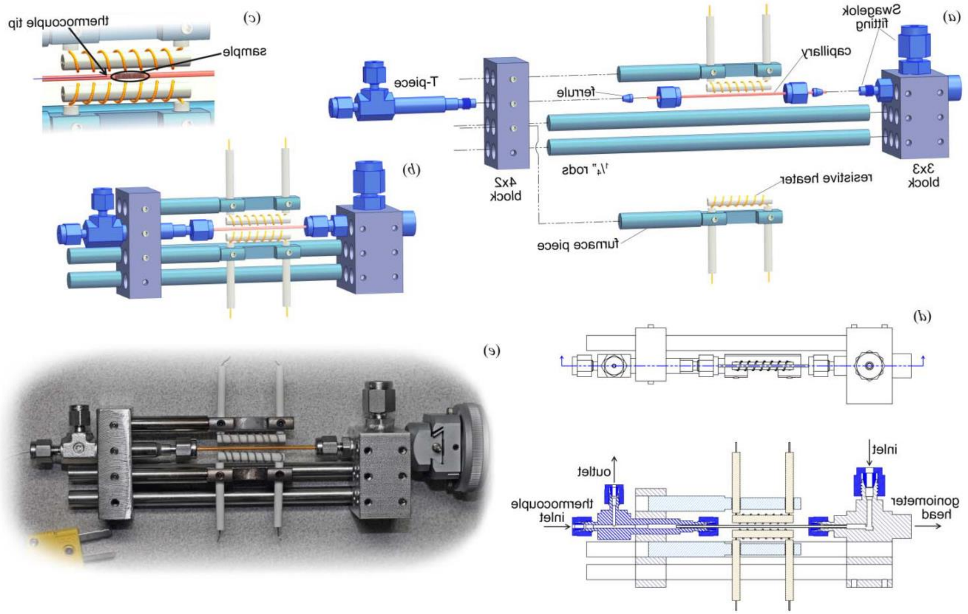
- Temperature and pressure control
- Structural characterization of intermediate compounds
- Gases in/out, flow control, analysis of gases out of the catalytic reaction

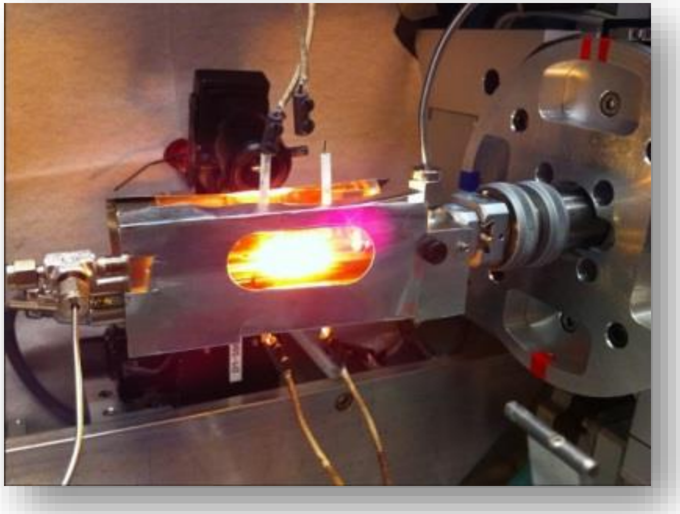
In-situ catalytic experiments

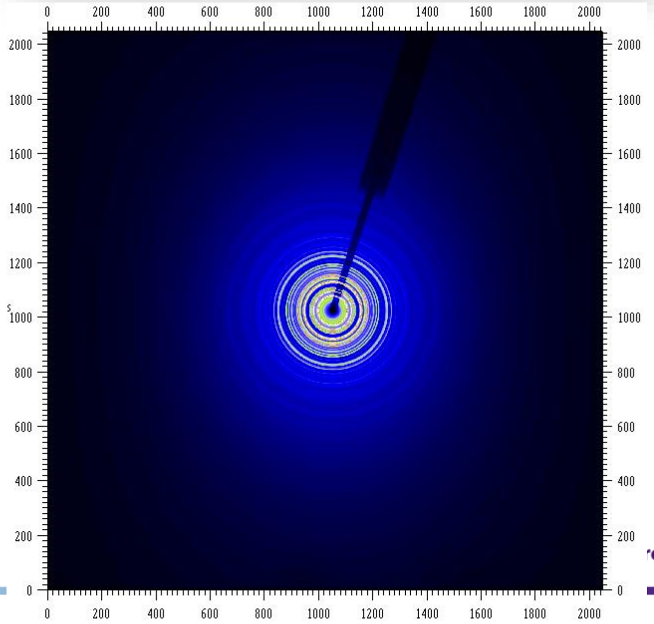
A versatile sample-environment cell for non-ambient X-ray scattering experiments

Peter J. Chupas,[a]* Karena W. Chapman,[a] Charles Kurtz,[a] Jonathan C. Hanson,[b]
Peter L. Lee[a] and Clare P. Grey[c]

J. Appl. Cryst. (2008). **41**, 822–824

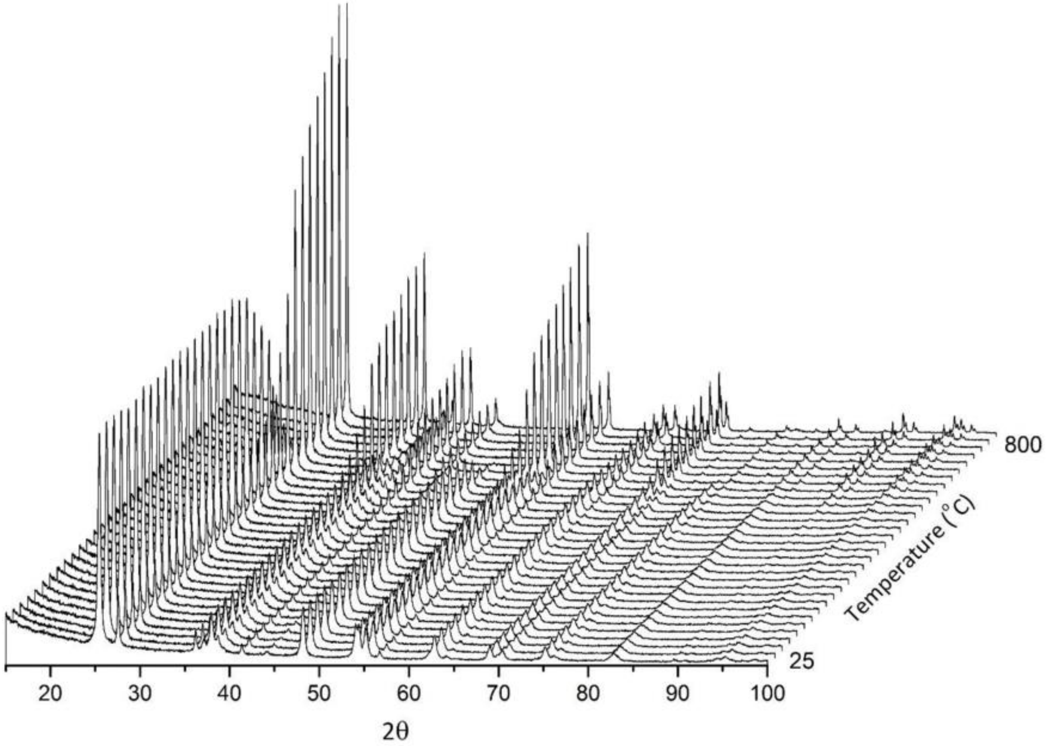


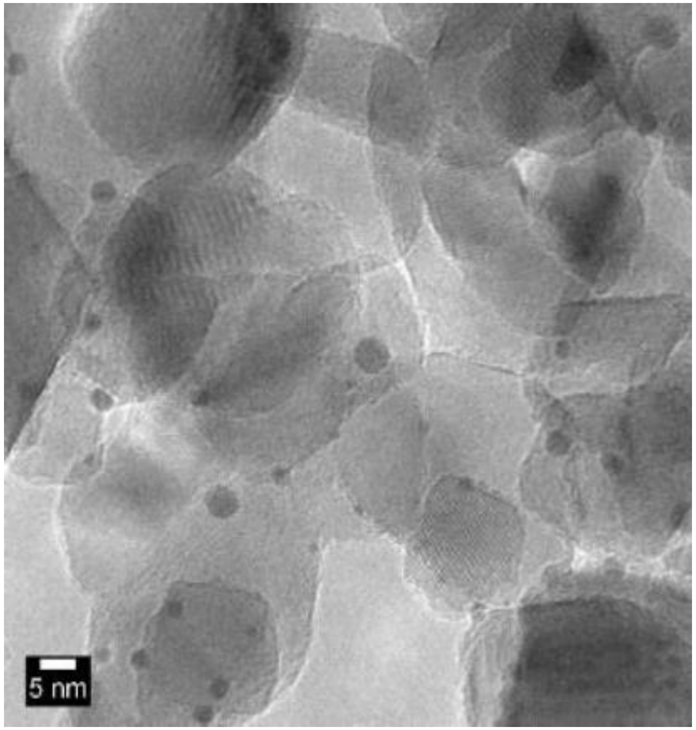




In-situ catalysis

Commercial catalyst Aurolite® (1% Au-P25)

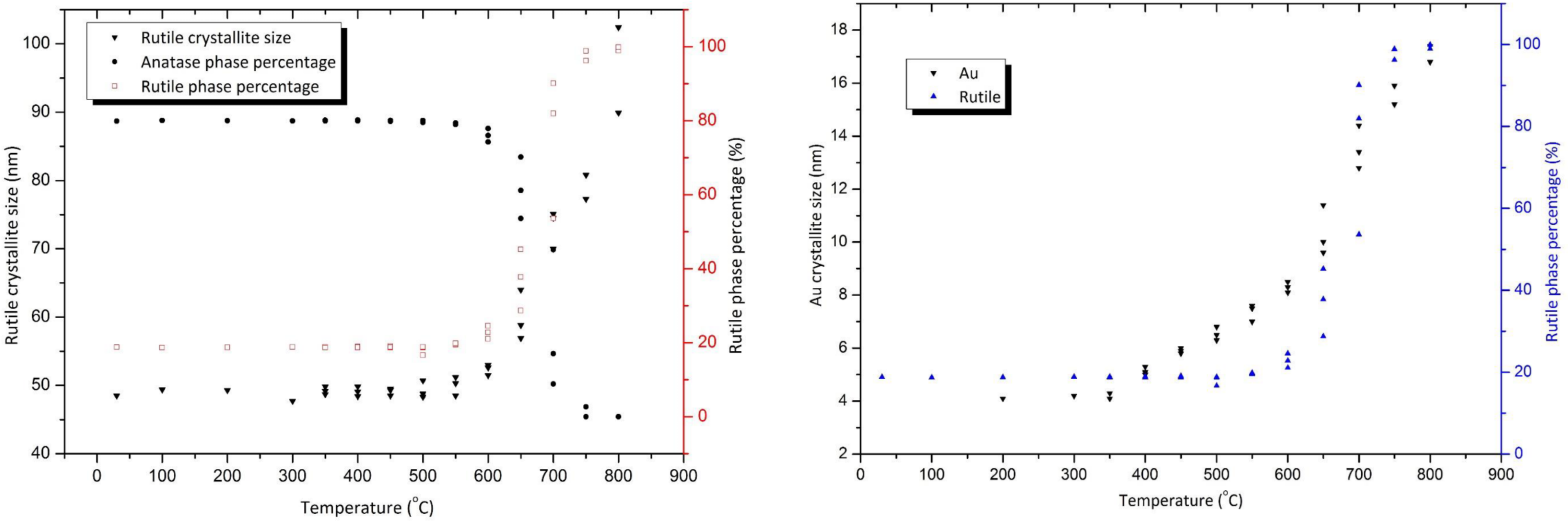




Phase change from anatase to the thermodynamically stable rutile phase

In-situ catalysis

Commercial catalyst Aurolite® (1% Au-P25)



Structural instability of the support is a major factor in Au-nanoparticle growth

→ catalytic activity decreases

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synchrotron

Achieving nano-gold stability through rational design†

D. Barret et al.

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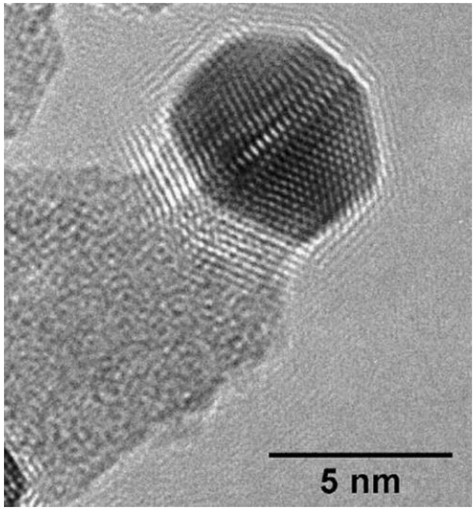
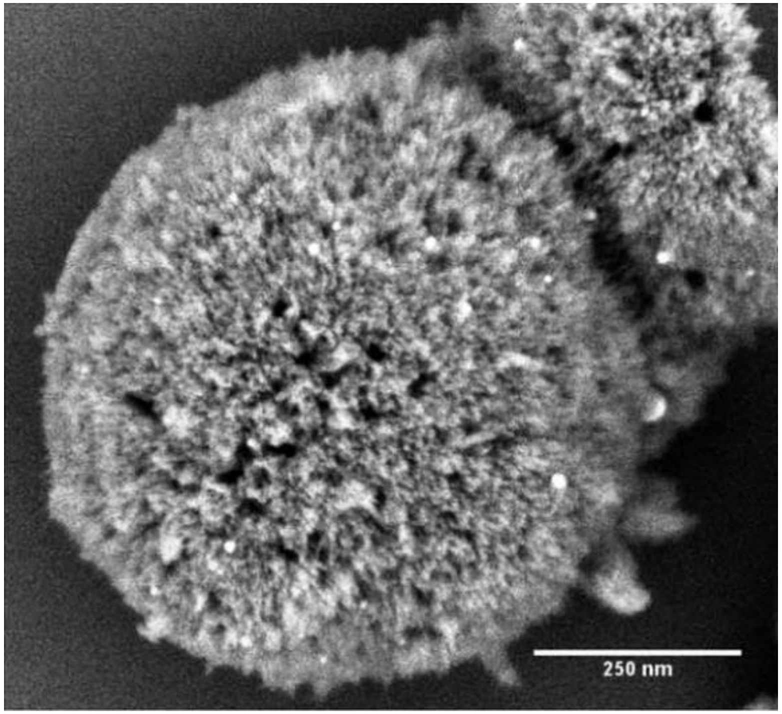
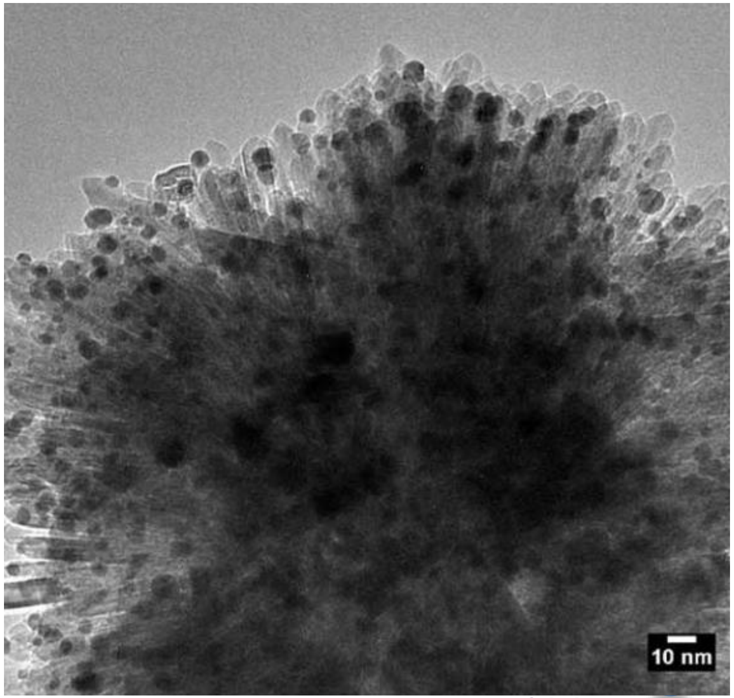
In-situ catalysis





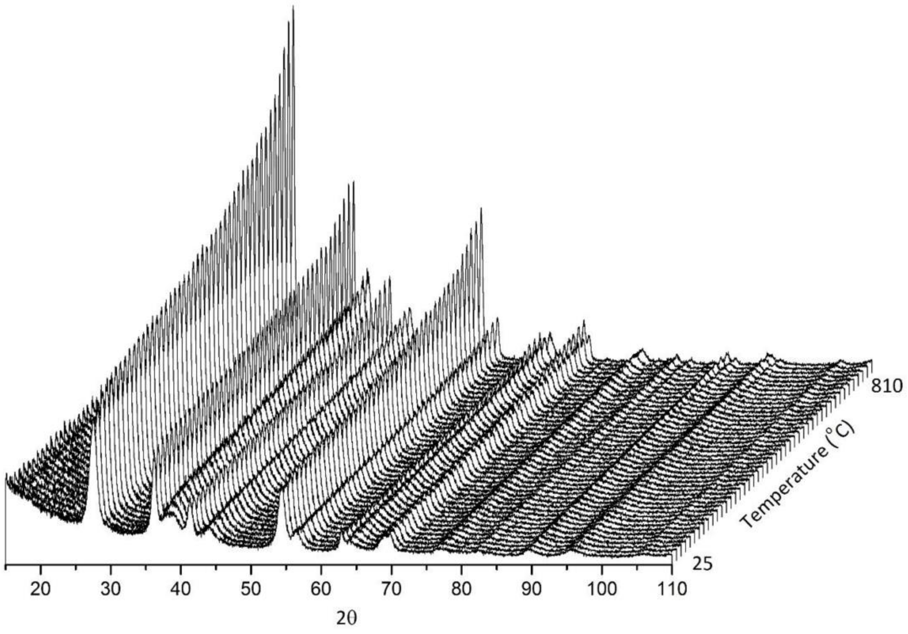


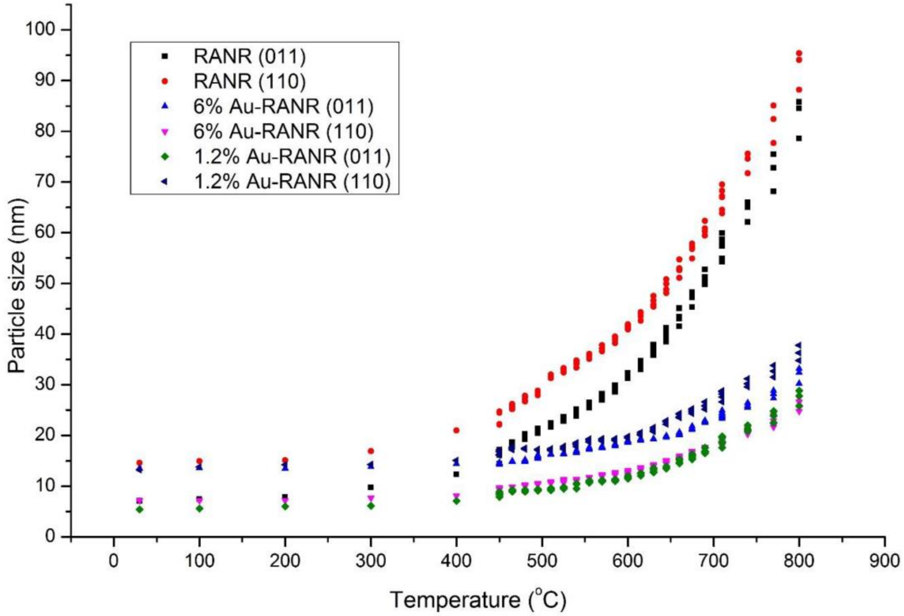
Achieving nano-gold stability through rational design†

D. Barret et al.

In-situ catalysis

The presence of Au resulted in a stabilizing effect with regards to the growth of the support structure.





Achieving nano-gold stability through rational design†

D. Barret et al.

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In-situ catalysis

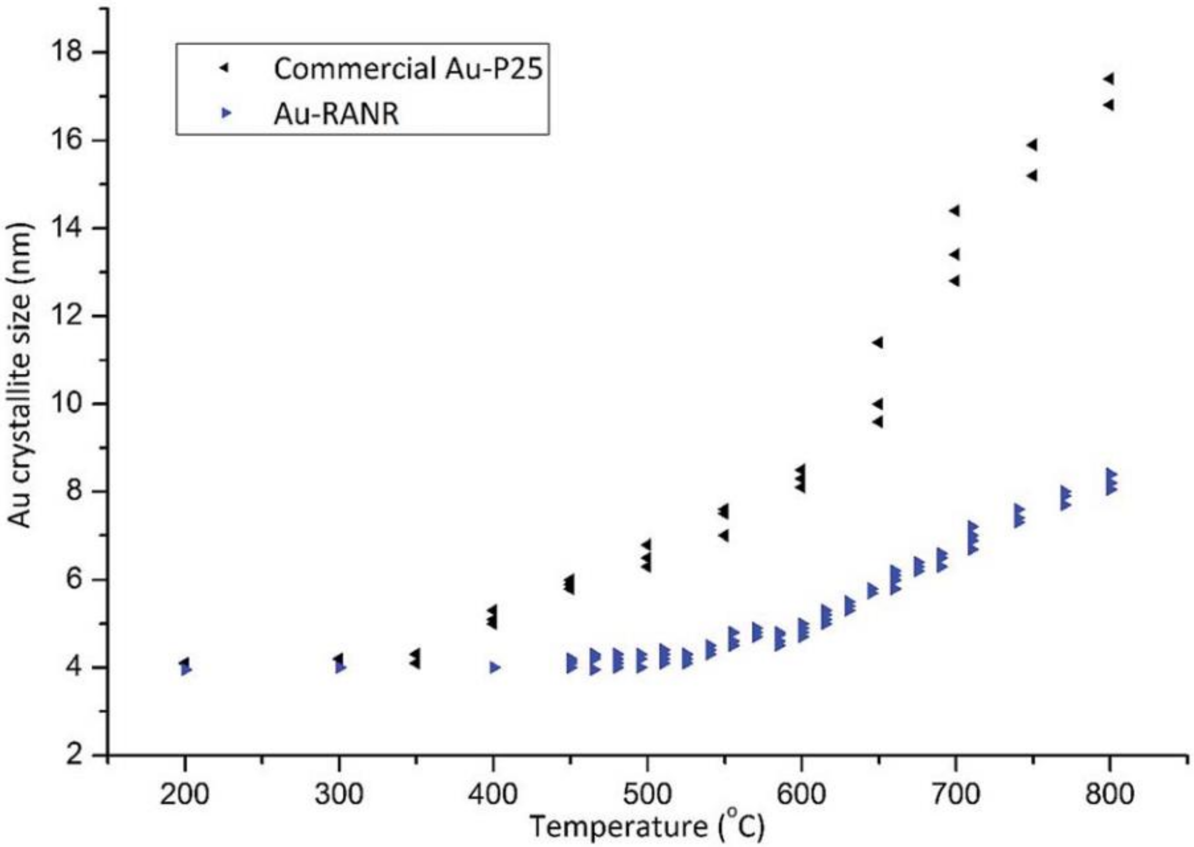

Fig. 3 Au crystallite sizes of the commercial Au–TiO_2 and Au-RANR catalysts determined from Rietveld refinement from *in situ* PXRD.

Achieving nano-gold stability through rational design†

D. Barret et al.

In-situ catalysis

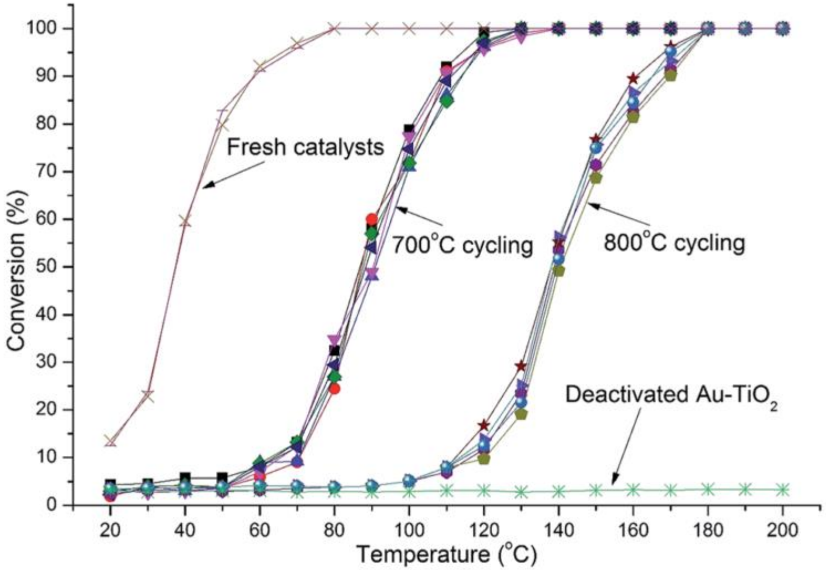

Fig. 4 Light-off curves for catalysts with 1.2% Au-RANR and commercial Au–TiO$_2$ after multiple 700 and 800 °C heating cycles (10 cycles in total).

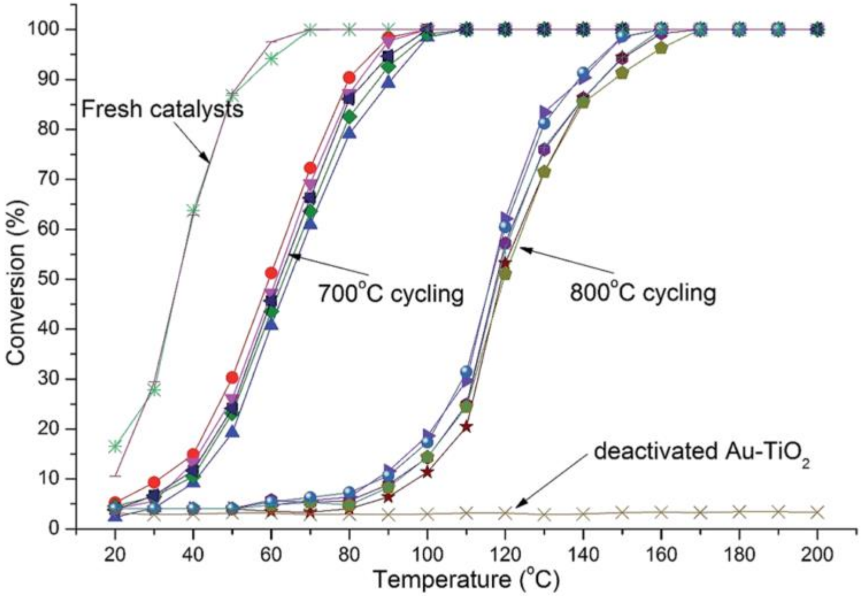

Fig. 5 Light-off curves for catalysts with 5% Au-RANR and commercial Au–TiO$_2$ catalyst after multiple 700 and 800 °C heating cycles (10 cycles in total).

- ✓ Thermodynamically stable support material
- ✓ Improved morphology
- ✓ Au nanoparticles sit isolated on the rod tips -> reduced mobility and coalescence
- ✓ Remarkable catalytic stability tested with CO oxidation

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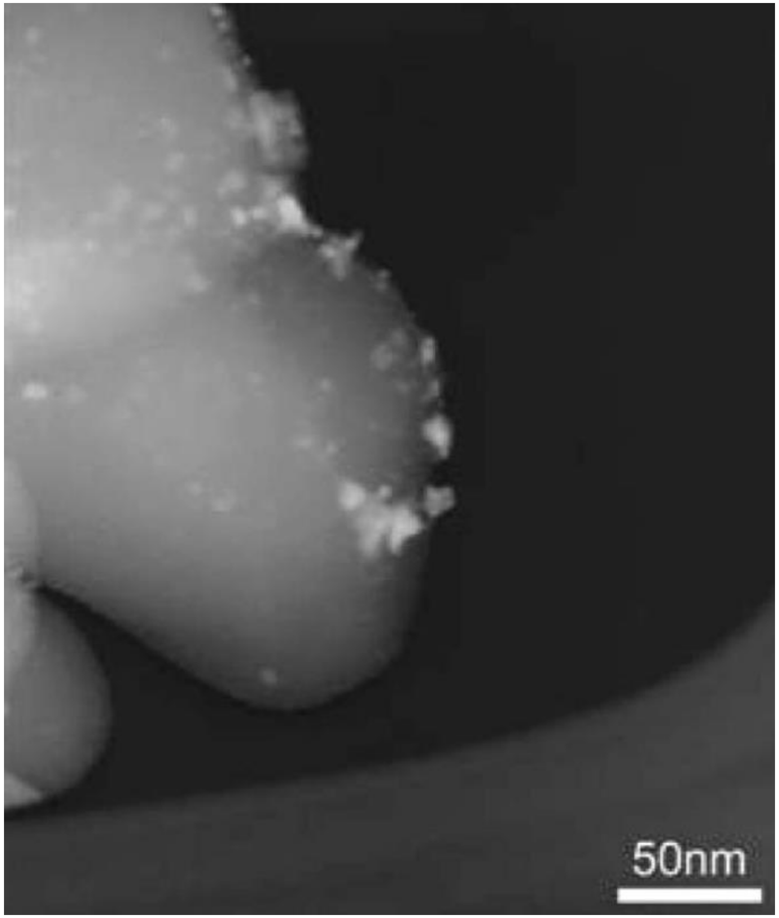
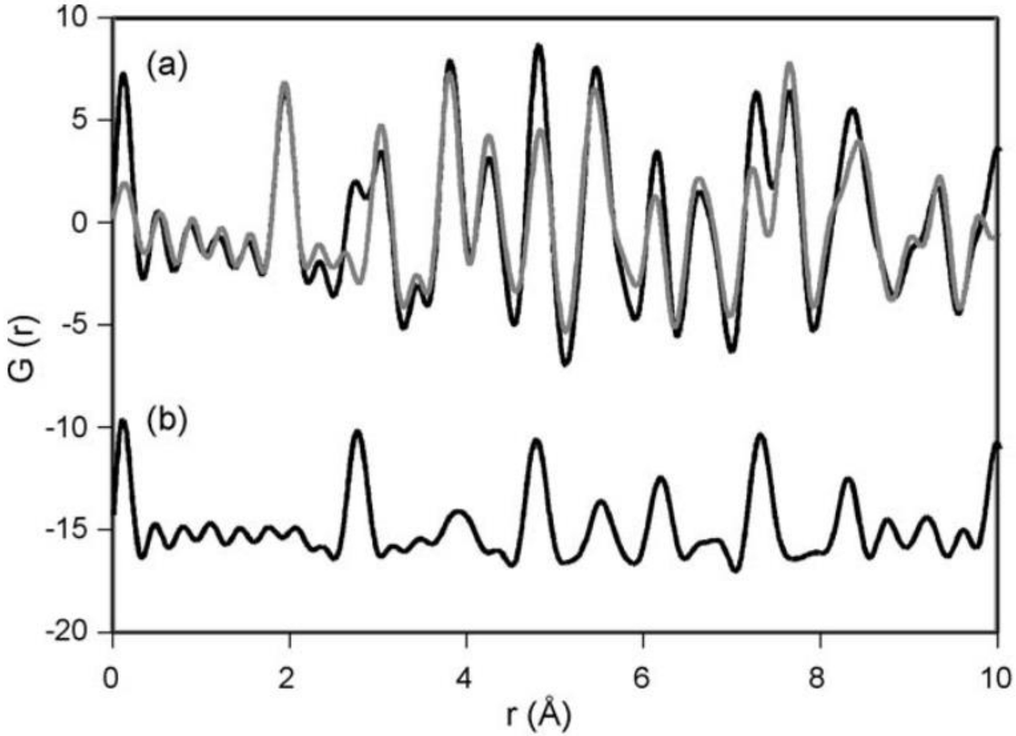
Achieving nano-gold stability through rational design†

D. Barret et al.

Application of high-energy X-rays and Pair-Distribution-Function analysis to nano-scale structural studies in catalysis

Peter J. Chupas [a,*], Karena W. Chapman [a], Hailong Chen [b], Clare P. Grey [b]





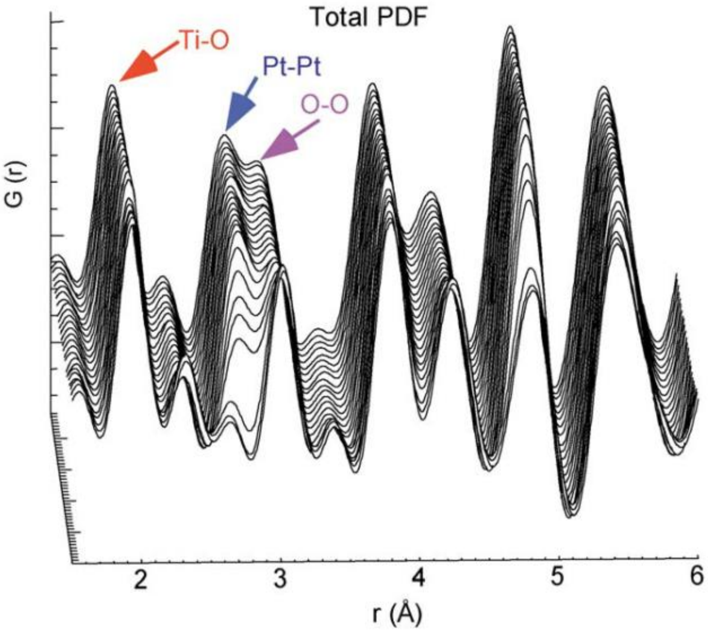
(a) Grey line: G(r) for TiO2 support

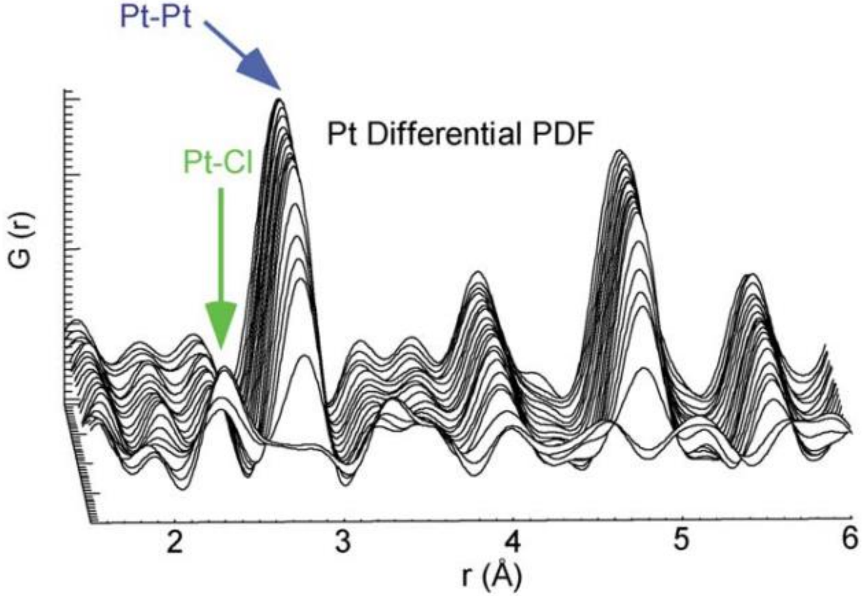
Black line: G(r) for 2.5% Pt on TiO_2 calcined under H_2 flow

(b) Differential PDF

Application of high-energy X-rays and Pair-Distribution-Function analysis to nano-scale structural studies in catalysis

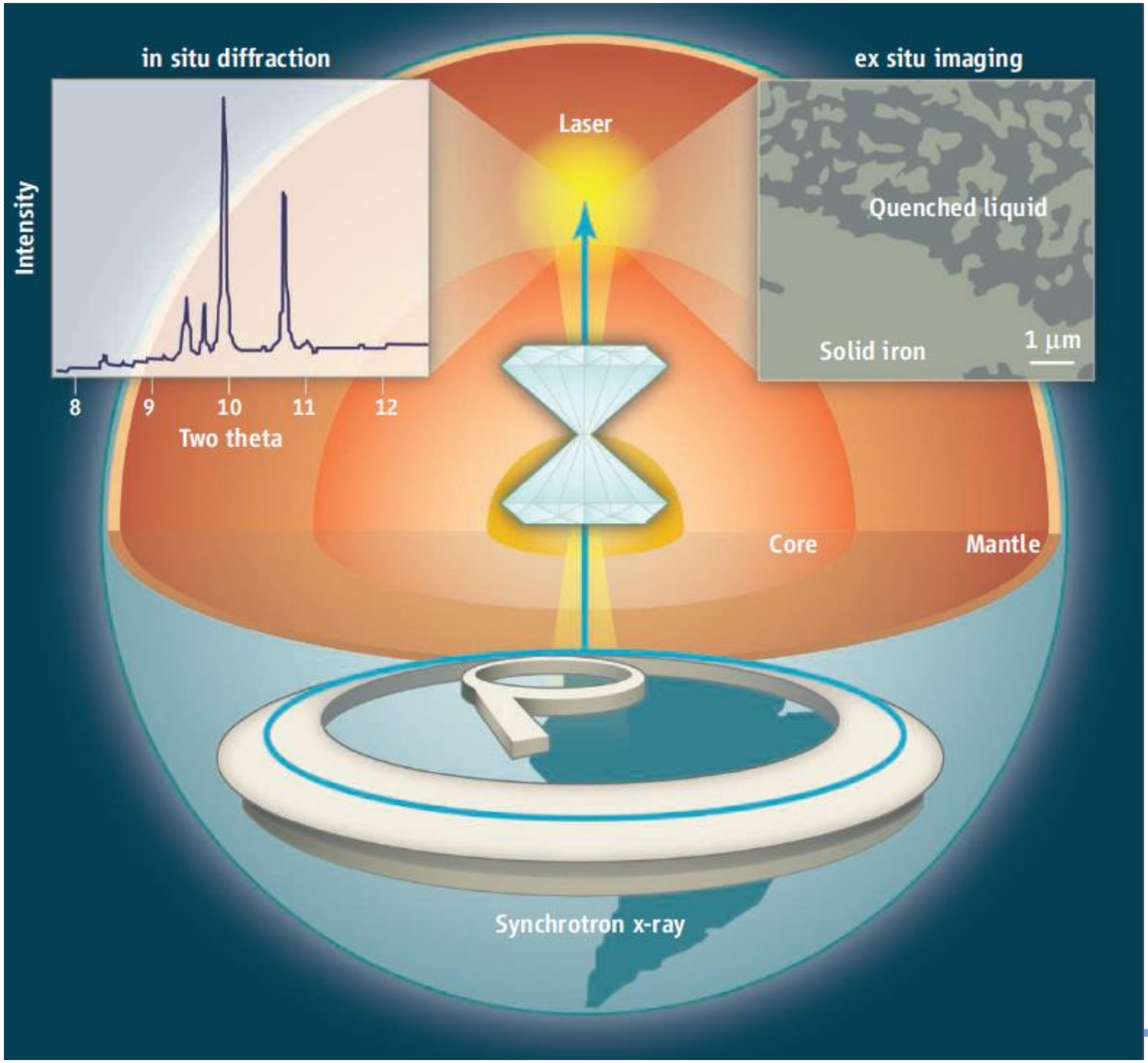
Peter J. Chupas [a,*], Karena W. Chapman [a], Hailong Chen [b], Clare P. Grey [b]





1. Pt nano-particles examined with atomic resolution
2. In-situ transformation of Pt^{4+}_ in PtCl$_6^{2-}$
3. Pt^{4+} reduced in situ with H$_2$ forming metallic fcc Pt nano particles
4. Observation of the Pt-O bond yields insight about catalyst interaction with TiO$_2$ support
5. Initial nano-particles are ~1nm, while by 200 °C they are larger and more crystalline
6. Suggests agglomeration of smaller particles to form larger particles

High pressure studies



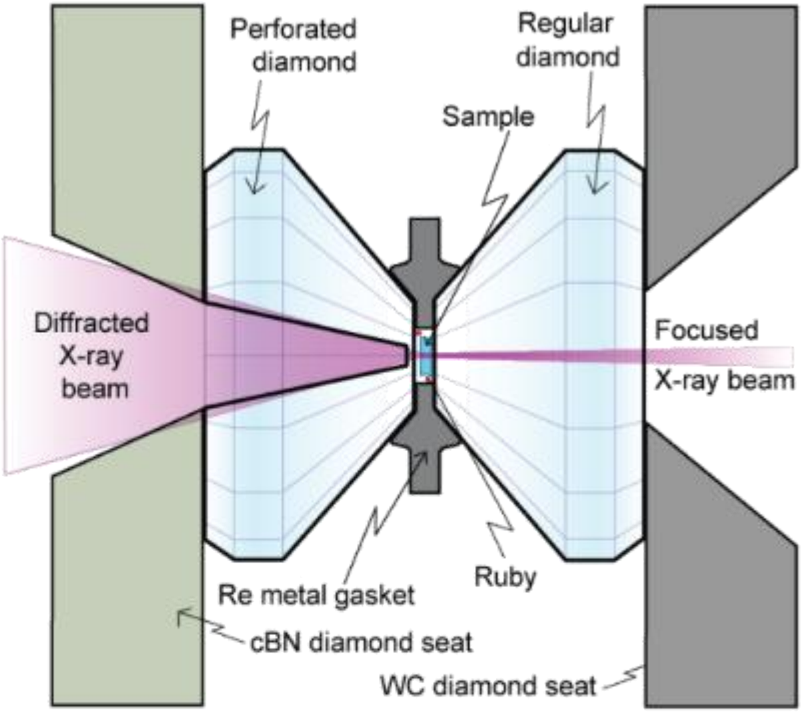
Probing extremes:

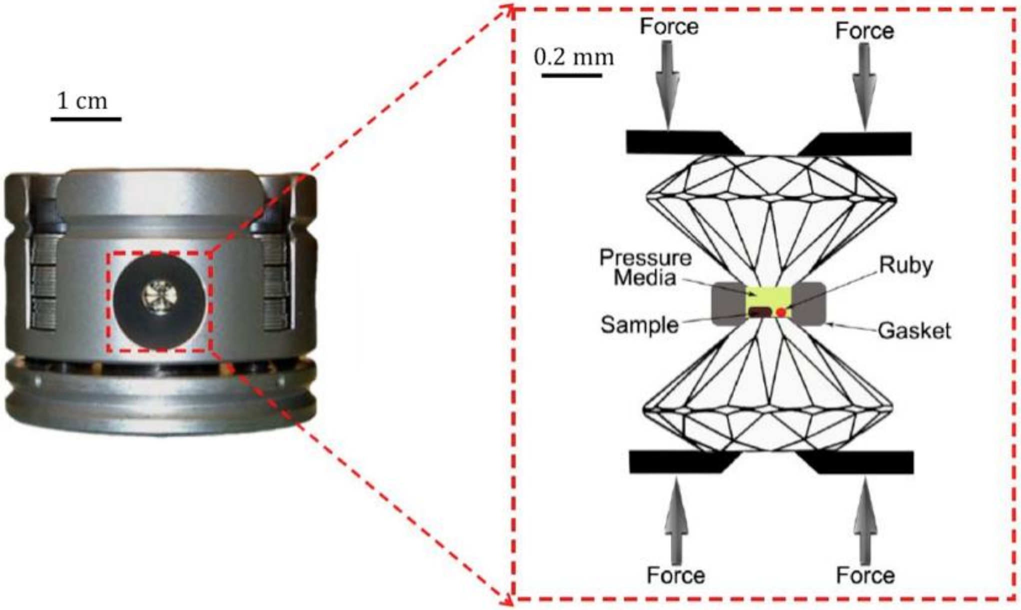
Melting Earth's core …

in the laboratory

Science **340**, 442 2013
Yingwei Fei

High pressure studies





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Combined high pressure and high temperature

Membrane Diamond Anvil Cell MDAC-THT

Spectroscopy at Medium-High Pressure & Very High temperature

These Membrane Diamond Anvil Cell are aimed at performing very high Temperature experiments at Medium-High Pressure.

Ref : [MDAC-x-THT]

Pressure range :
0 to 1 Mbar (depending on the culet size of the diamonds).

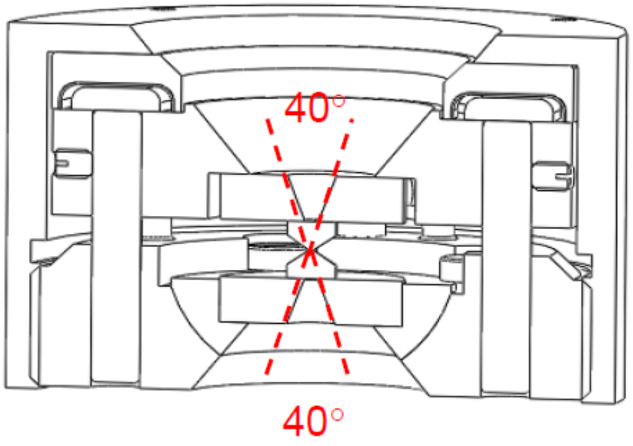
Temperature range :
- Room temperature to 1000 K.

Optical access to sample :
Full angle apertures 40° to 76°max/40° to 76°max (optional).
Working distance 13mm.

Accessible electromagnetic spectrum :
Visible, X rays, Raman, Infrared (with specific diamonds) .

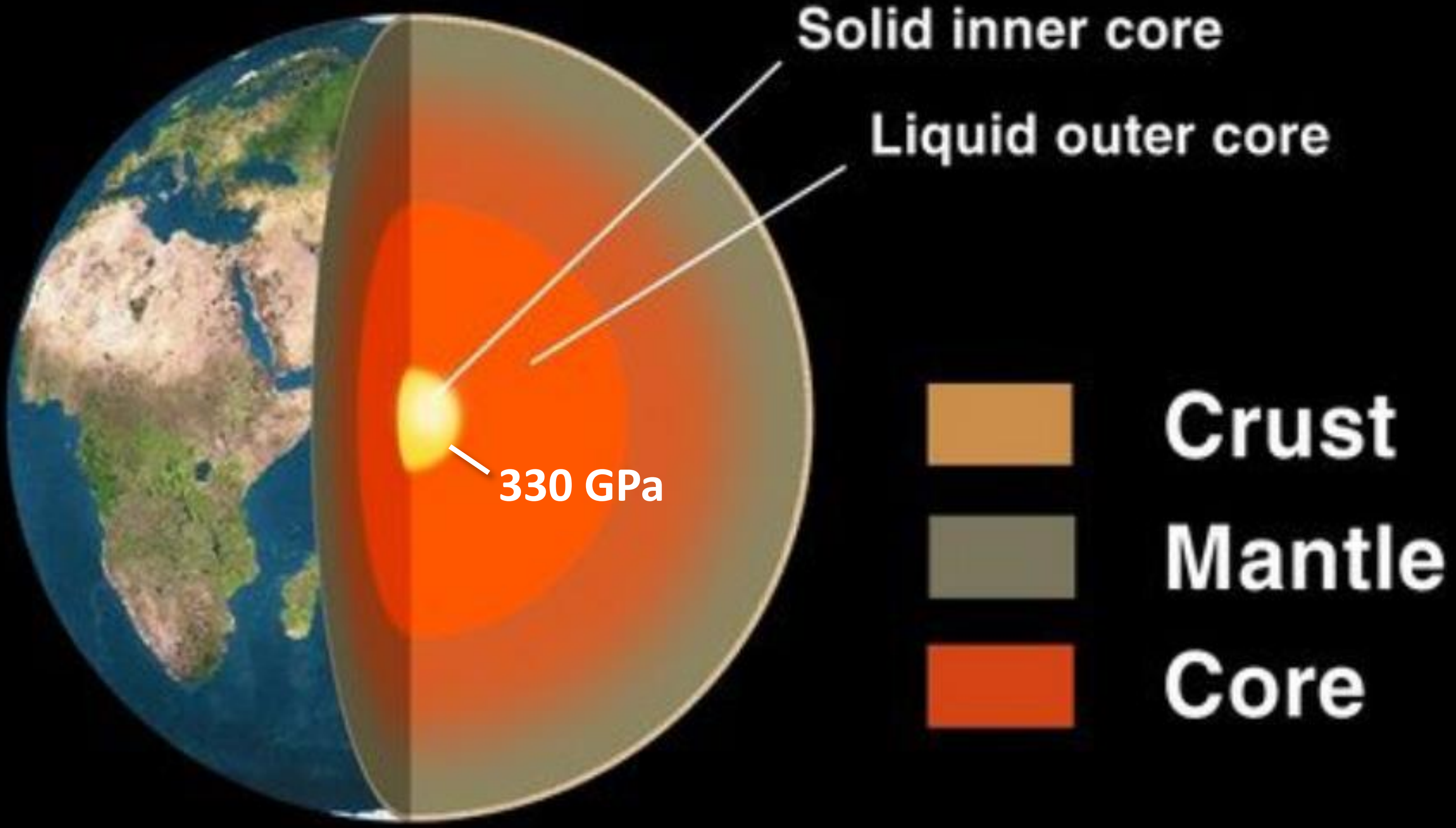
Materials :
Super Alloys & High Temperature super hard seat.

Sizes/ Weight :
Height 32mm (1.26”), Diameter 50mm (1.97”).125 g (0.288 lbs).



2 diamonds height 1,5mm / 2 diamonds height 2,5mm / cylindrical seat / Laser heating

Earth’s core is structured in a solid inner core, mainly composed of iron, and a liquid outer core.

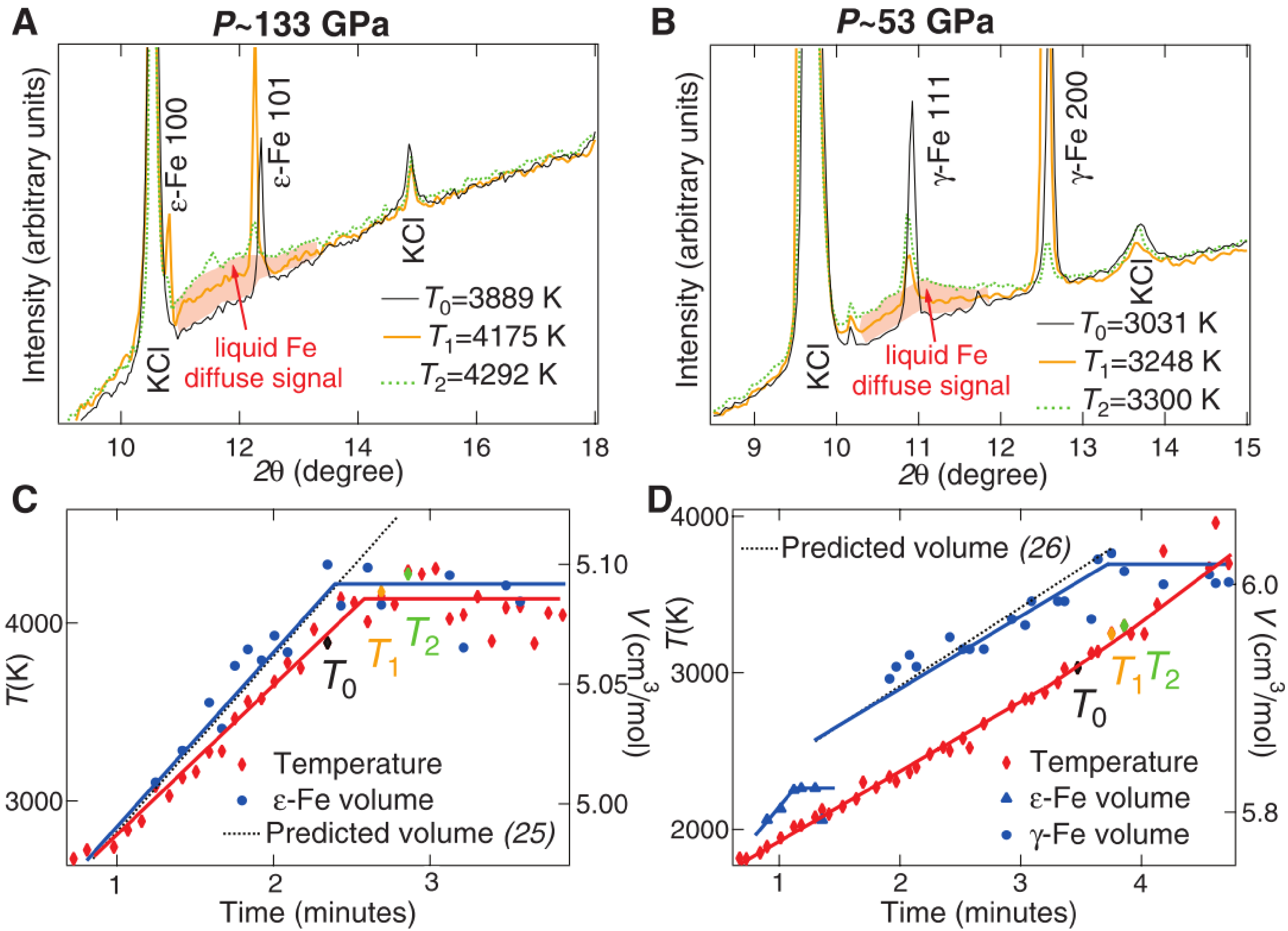


How does iron behave at these extreme temperatures and pressures?

Anzellini, Science 340, 464, 2013

Melting of Iron at Earth's Inner core Boundary based on Fast X-ray Diffraction

Static laser-heated diamond anvil cell experiments up to 200 GPa



4000 K = 3727 °Celsius

1 GPa = 9869 atm

Science **340**, 464, 2013. Anzellini et al.

Melting of Iron at Earth’s Inner core Boundary based on Fast X-ray Diffraction

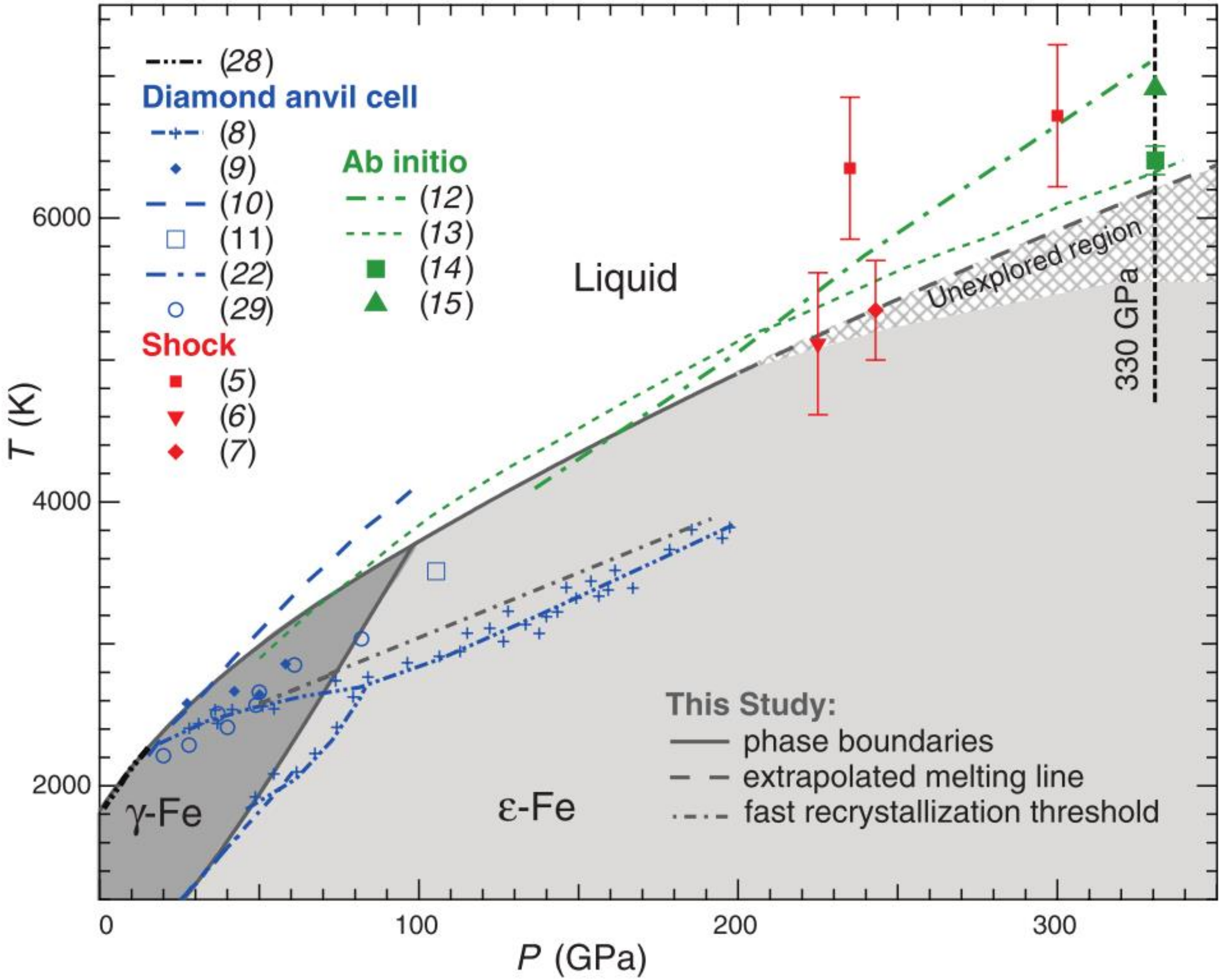
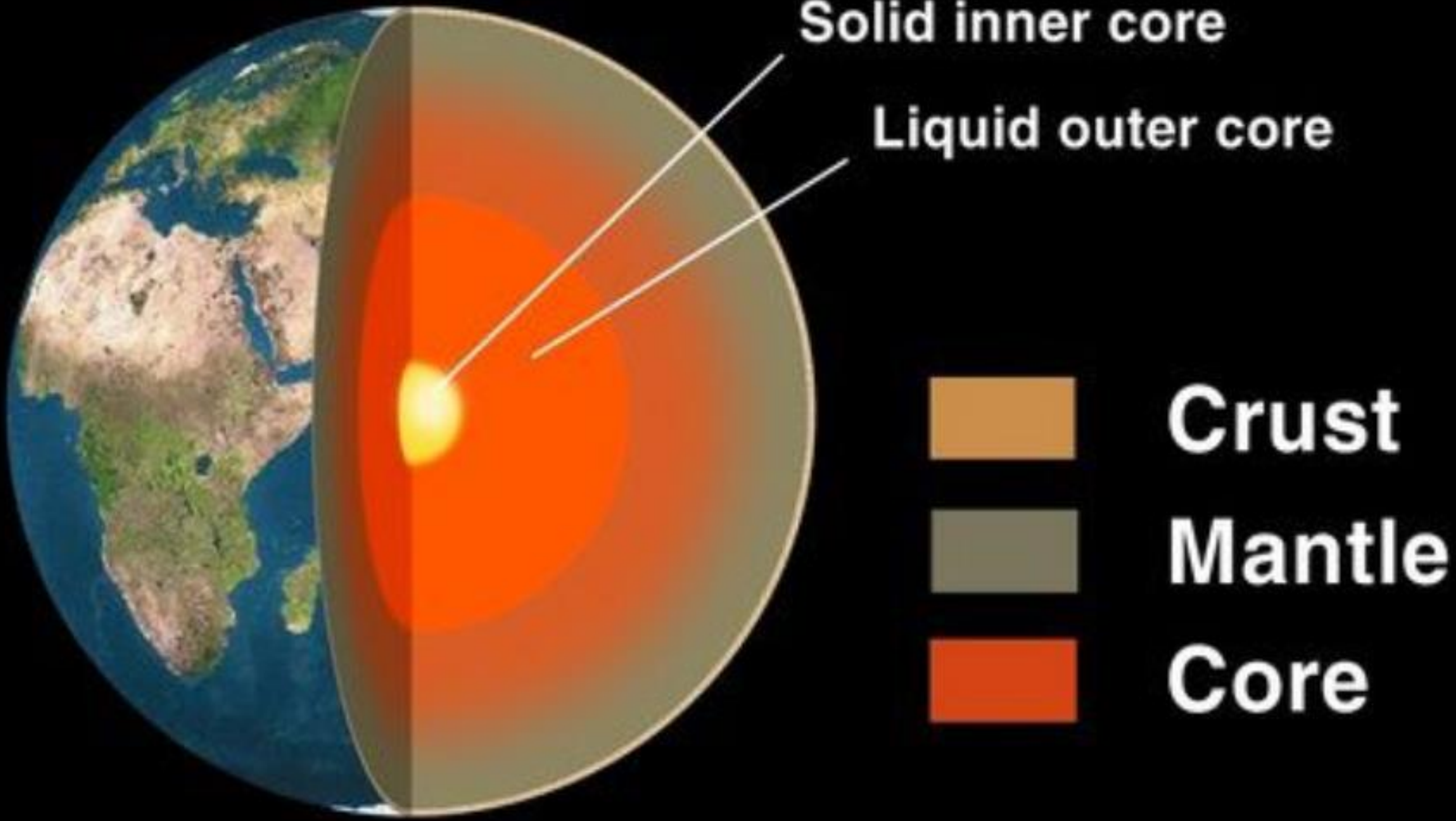


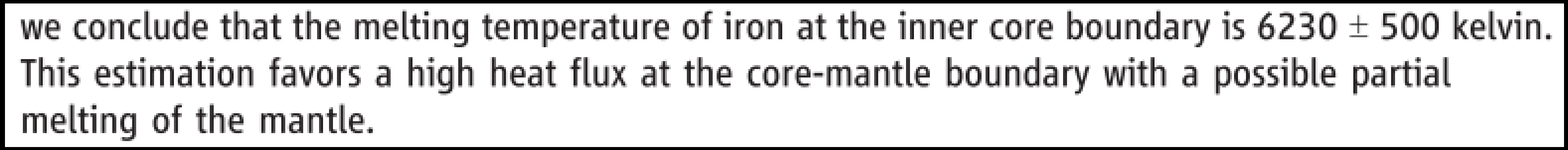
Fig. 3. Phase stability domains for Fe obtained in the literature and in this study. The stability field for ε-Fe is based on the current study data and data from (*19*).

tsource.ca

lini et al.

Earth's core is structured in a solid inner core, mainly composed of iron, and a liquid outer core.





we conclude that the melting temperature of iron at the inner core boundary is 6230 ± 500 kelvin. This estimation favors a high heat flux at the core-mantle boundary with a possible partial melting of the mantle.

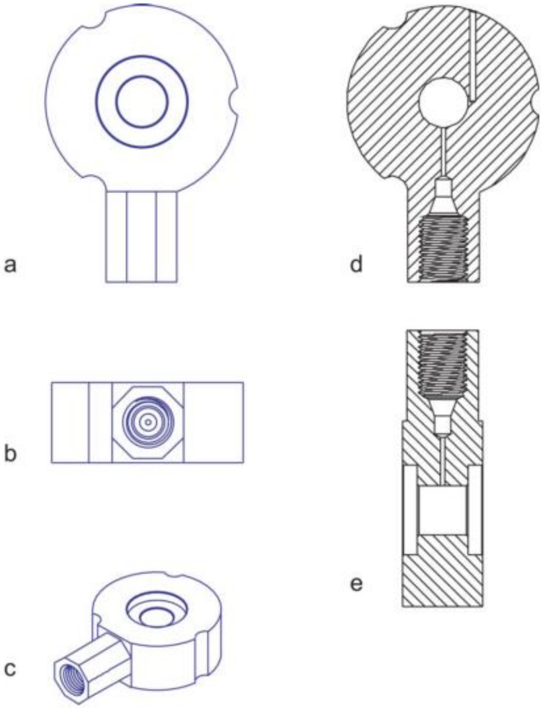
1811 K
at 1 bar

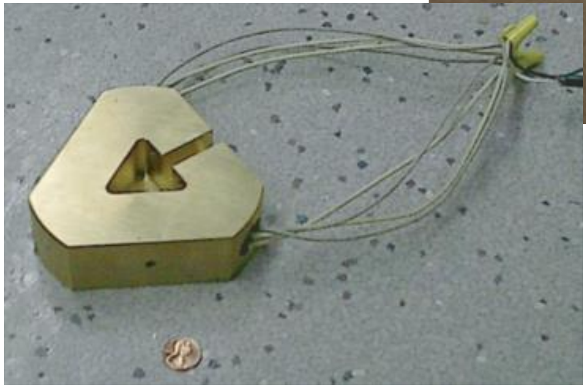
Anzellini, Science 340, 464, 2013

Externally controlled pressure and temperature microreactor for *in situ* x-ray diffraction, visual and spectroscopic reaction investigations under supercritical and subcritical conditions

Microreactor for pressure and temperature control

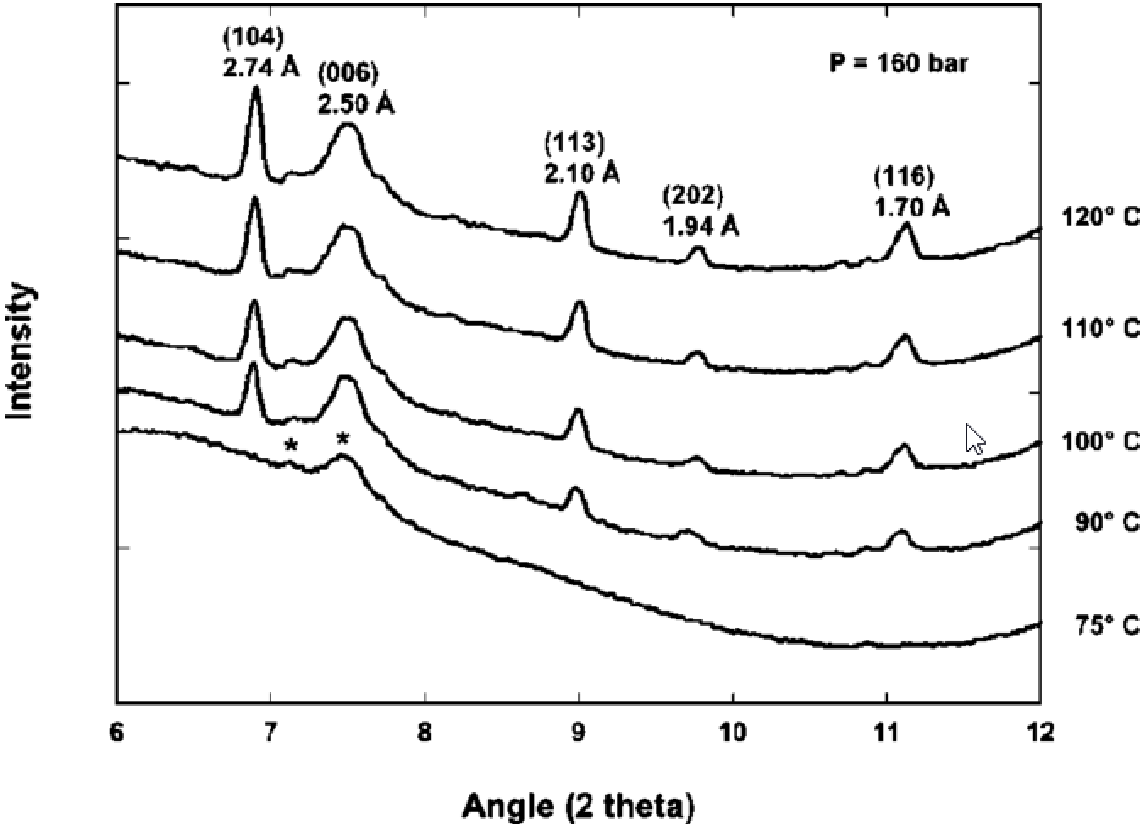
- In-Situ XRD and XAS experiments
- From ambient to up to 400 ^{o}C and 310 bar (external control)
- ✓ Structural studies
- ✓ in situ reaction processes





Diefenbacher, Rev. Sci. Instrum. **76**, 015103 (2005)

Externally controlled pressure and temperature microreactor for *in situ* x-ray diffraction, visual and spectroscopic reaction investigations under supercritical and subcritical conditions



Conversion of a meta-serpentine sample to magnesite under high pressure and temperature

$$Mg_3Si_2O_{6.32}(OH)_{1.36} + 3CO_2$$
$$- > 3MgCO_3 + 2SiO_2 + 0.68H_2O$$

Carbonation of serpentine:

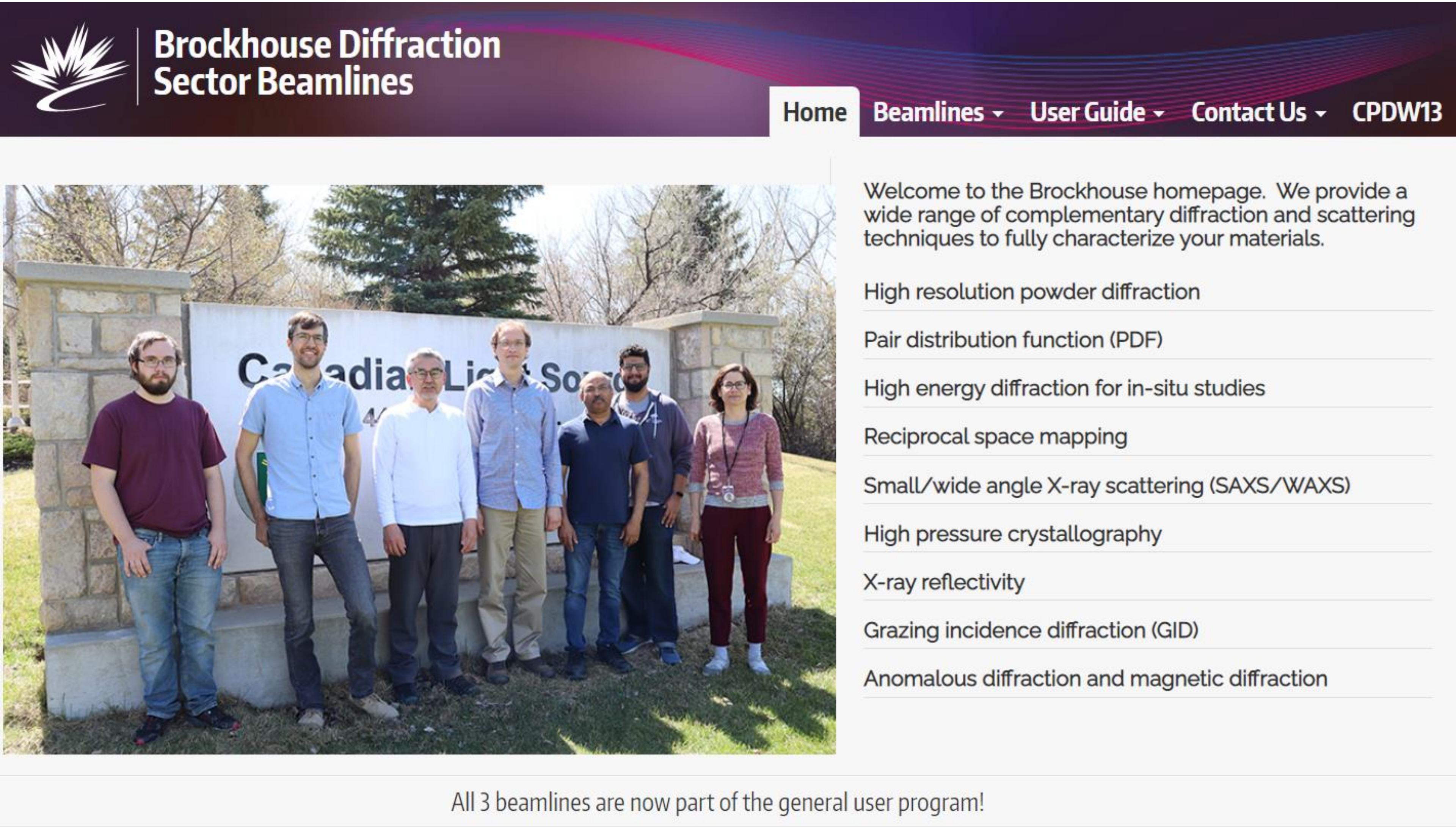
- 100,000 years for nature
- 1h with this high P/T setup

Jason Diefenbacher, Rev. Sci. Instrum. **76**, 015103 (2005)

Conclusions

- In-situ experiments allow to study the materials and components under working conditions
- They yield very important information about the processes, facilitating the improvement of the materials and devices
- Many options exist both for in-house diffractometers and synchrotrons
- Synchrotrons are very flexible and well suited for in-situ experiments.

brockhouse.lightsource.ca



Brockhouse Diffraction Sector Beamlines

Welcome to the Brockhouse homepage. We provide a wide range of complementary diffraction and scattering techniques to fully characterize your materials.

- High resolution powder diffraction
- Pair distribution function (PDF)
- High energy diffraction for in-situ studies
- Reciprocal space mapping
- Small/wide angle X-ray scattering (SAXS/WAXS)
- High pressure crystallography
- X-ray reflectivity
- Grazing incidence diffraction (GID)
- Anomalous diffraction and magnetic diffraction

All 3 beamlines are now part of the general user program!

beatriz.moreno@lightsource.ca

Acknowledgments