# *Synchrotron X-Ray Studies of Solid Oxide Fuel Cell Materials*

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# *Experimental Summary*

- **Controlled Atmosphere Experiments**
  - Sr surface segregation in LSM is observed at all temperature and $pO_2$ conditions
  - The dependence of Sr surface segregation is consistent with a charge neutralization mechanism for both oxygen vacancies and the polar LSM surface

- **Electrochemical Experiments**
  - Strong indication of Sr segregation at room temperature in LSM.
  - Sr segregation goes down at high temperature and goes up at room temperature even after fast cooling (700°C to RT in 30 min).
  - Changes in Co K edge XANES in LSC with heating but no significant change by electrochemistry.
  - Cathodic or anodic polarizations may control the Sr segregation and desegregation rates.
  - Full-cell experimental design in development.

# *Team Members*

- **Materials Science, ANL**
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  - Dillon Fong
  - Jeffrey Eastman
- **Chemical Sciences and Engineering, ANL**
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  - J.C. Meador
- **Massachusetts Institute of Technology**
  - Bilge Yildiz
  - Burc Misirlioglu

# *Overview*

**Operating fuel cells are complex devices with challenging materials problems.**

- **Greatest efficiency loss in SOFC occurs at cathode;**
  - developing efficient, cost-effective cathodes reduces capital costs, benefiting the customer.
- **High operating temperature decreases life time of cathode materials;**
  - developing SOFCs working at lower operating temperatures can greatly enhance stability, thereby reduce overall cost to the customer.

# Overview

**Theory of atomic-scale processes**

**Operating solid oxide fuel cell cathode**

***Challenge: How to deal with the many complex atomic-scale processes governing cathode performance?***

# Overview

**Theory of atomic-scale processes**

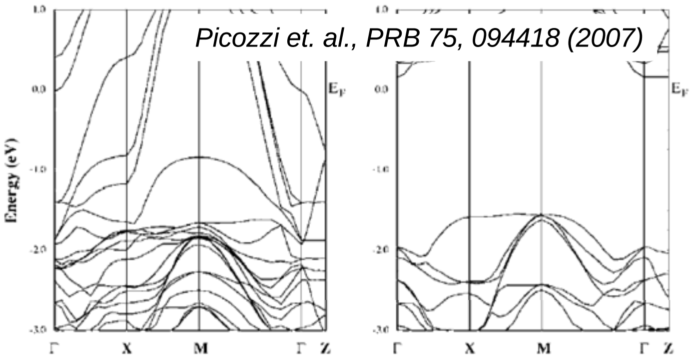
- **Ex situ studies of both model and realistic systems**
- **In situ studies of both model and realistic systems**
  - **controlled T and $pO_2$**
  - **half-cell operation**
  - **full-cell operation**

**Operating solid oxide fuel cell cathode**

***Solution: Combination of in situ and ex situ measurements to bridge gap between theory and technology, leading to design of new cathode materials***

# *Synchrotron Science's role in SECA*

*ex situ* atomic resolution microscopy




Theory for current and future materials

Synchrotron Studies

*In situ* measurements at working conditions: high T, $pO_2$, & electrochemistry

- **Comparing *in situ* and *ex situ***
- **Providing basis for theoretical modeling**
  - Improve understanding of cathode materials, while paving way for future SOFC innovation

# *Synchrotrons Have Revolutionized X-Ray Analysis*

- **The Advanced Photon Source is nine orders of magnitude brighter than laboratory sources.**
- **Brightness has enabled:**
  - Scattering from single layers of atoms
  - Nanometer resolution imaging
  - Realtime, *in situ* measurements from all types of surfaces and ultra-thin films
  - Structure determination of buried interfaces
- **Great potential for advancing understanding of complex industrial processes.**

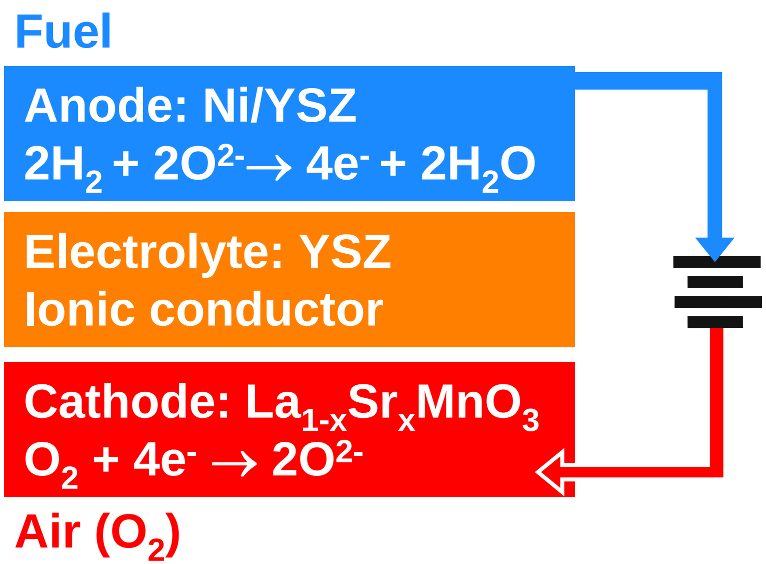
# *In Situ Synchrotron Studies*

**In situ studies employ synchrotron x-ray scattering and spectroscopy tools. These techniques probe atomic-scale processes under SOFC operating conditions.**

- **In Situ Controlled Atmosphere Studies**
  - Equilibrium structure in controlled atmosphere (e.g. variable T and $pO_2$).
  - Identify driving forces for structural and chemical rearrangement
- **In Situ Electrochemical Studies**
- **In Situ Studies of Operating Fuel Cells**

# Motivation for Controlled Atmosphere Experiments

- Previous studies using angle-resolved x-ray photoelectron spectroscopy have observed strontium surface segregation under room temperature vacuum conditions.
- Interplay between strontium segregation and oxygen vacancies at operating temperature and potential may be important factor for oxygen reduction.



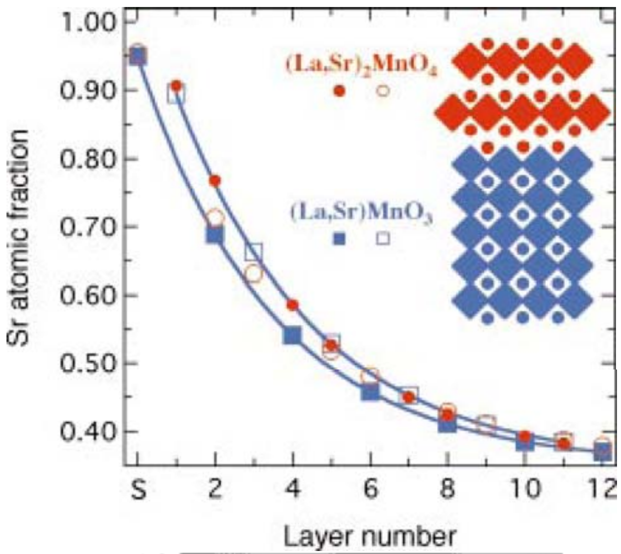

Determine the surface structure, reactions and thermodynamics of SOFC cathodes (e.g. $La_{1-x}Sr_xMnO_3$ (LSM) and $La_{1-x}Sr_xCoO_3$ (LSC) under controlled temperature, electrochemical potential, and gas partial pressures.

# Previous Results

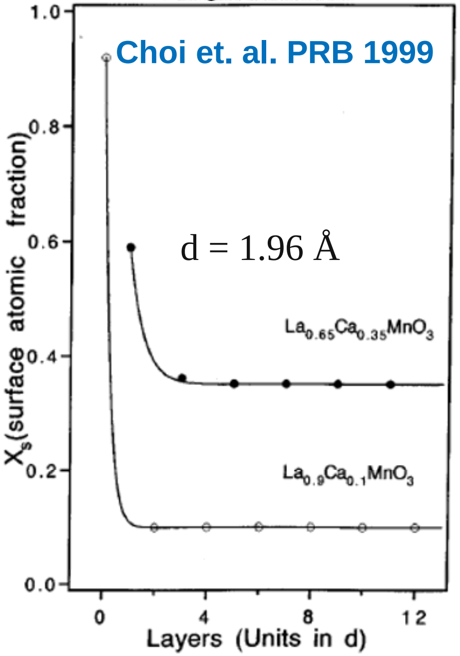
- Choi et. al. (PRB, 2006): Finds Ca surface segregation in $La_{1-x}Ca_xMnO_3$ thin films using XPS.
- Dulli et. al. (PRB, 2001): Influenced by Choi, uses angle-resolved x-ray photoelectron spectroscopy (XPS) on 001 LSM, finds Sr surface segregation with exponential decay to bulk.
- Jiang et. al. (SSI 2001): Finds evidence Sr segregation using acid etch. Performance improves following acid etch.
- Mannella et. al. (J. App. Phys. 2003): XPS shows no evidence Sr surface segregation at T = 135-500K.
- de Jong et al (J. App. Phys. 2003): XPS shows similar Sr enrichment as Dulli et al; suggests a surface layer of SrO or $SrCO_3$ is present.
- Kumigashira et. al. (App. Phys. Lett. 2003): Finds Sr surface segregation in LSM thin films using XPS.
- Wu et. al. (Mat. Lett. 2005): Finds Sr surface segregation with XPS.
- Caillol et. al. (App. Sur. Sci. 2007): XPS shows Sr enrichment in screen-printed LSM.

**All work done in non-equilibrium conditions.**

Dulli et. al. PRB 2001

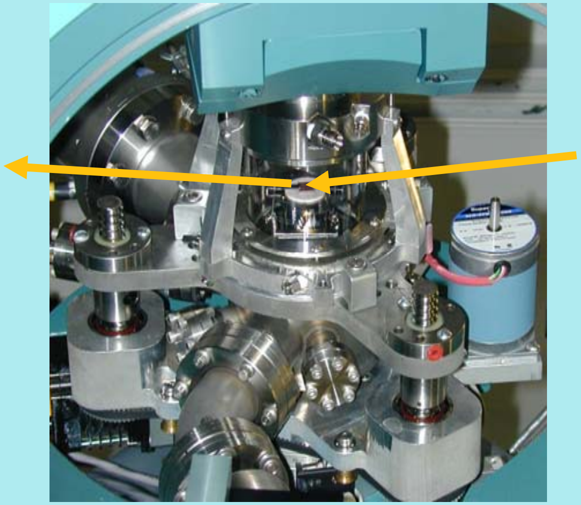



Choi et. al. PRB 1999



# Approach

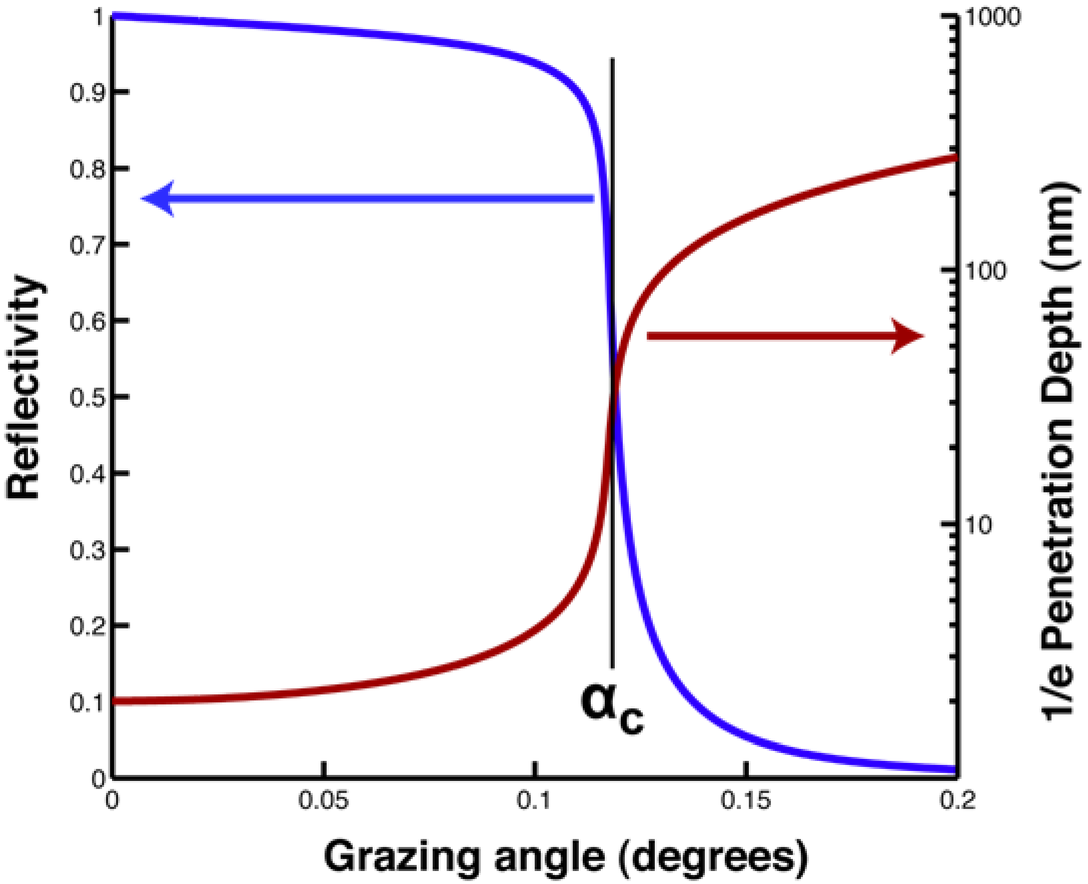
- **LSM and LSC epitaxial films grown by Pulsed Laser Deposition (PLD) at Carnegie Mellon University**
  - Growth: 750°C, 50 mTorr $O_2$, $La_{0.7}Sr_{0.3}MnO_3$ and $La_{0.7}Sr_{0.3}CoO_3$
  - Cooled in 300 Torr $pO_2$
  - (001) $SrTiO_3$ (STO), (110) $NdGaO_3$ (NGO) & $DyScO_3$ (DSO) substrates provide different epitaxial strain conditions
  - Yittria-Stabilized Zirconia (YSZ) (111) single crystal substrates for electrochemical measurements
- **In situ synchrotron x-ray studies**
  - Probes atomic-scale processes during realistic SOFC conditions
  - Studies performed at the Advanced Photon Source
  - Total reflection x-ray fluorescence (TXRF) to determine surface composition
  - Grazing incidence & high angle diffraction to determine surface and film structure



- Portable environmental chamber; mounts on 6-circle diffractometer @ APS Sectors 12 or 20
- Base pressure ~$10^{-7}$ Torr; $pO_2$ control by precise mixing of purified gases; monitor with RGA
- 24 keV x-rays
- T ≤ 1000°C

# *Total Reflection - Making X-rays Surface Sensitive*

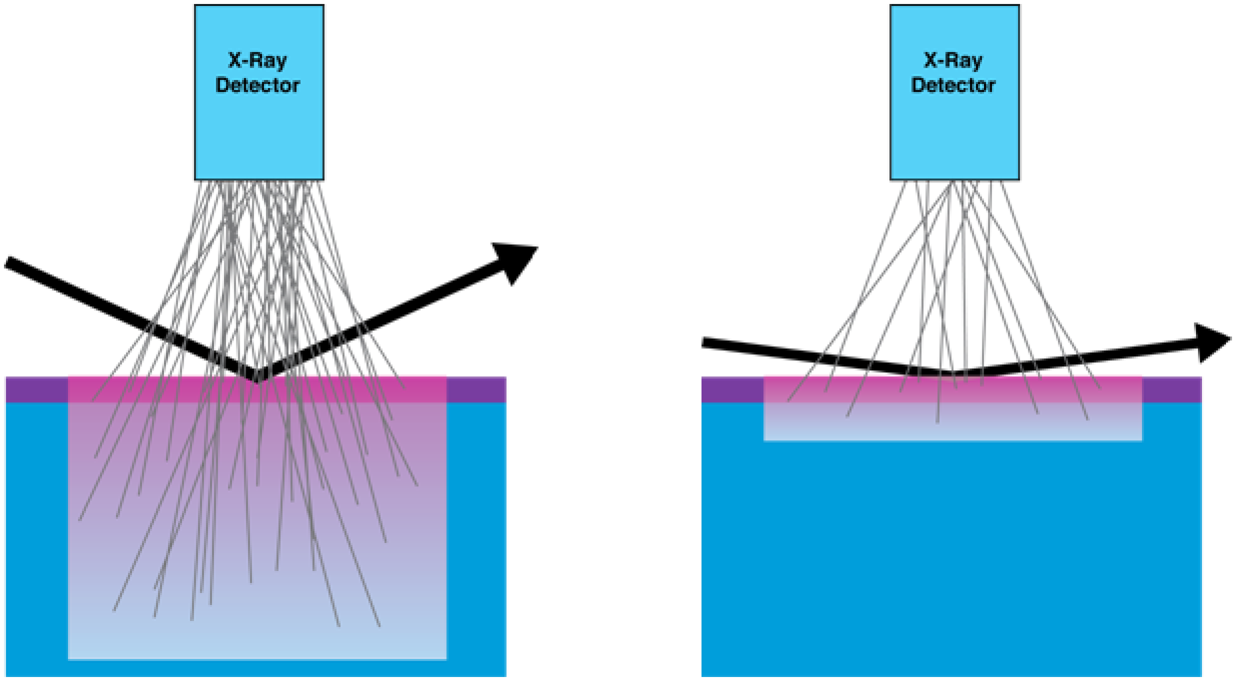
**$La_{0.7}Sr_{0.3}MnO_3$ using 24 keV Photons**



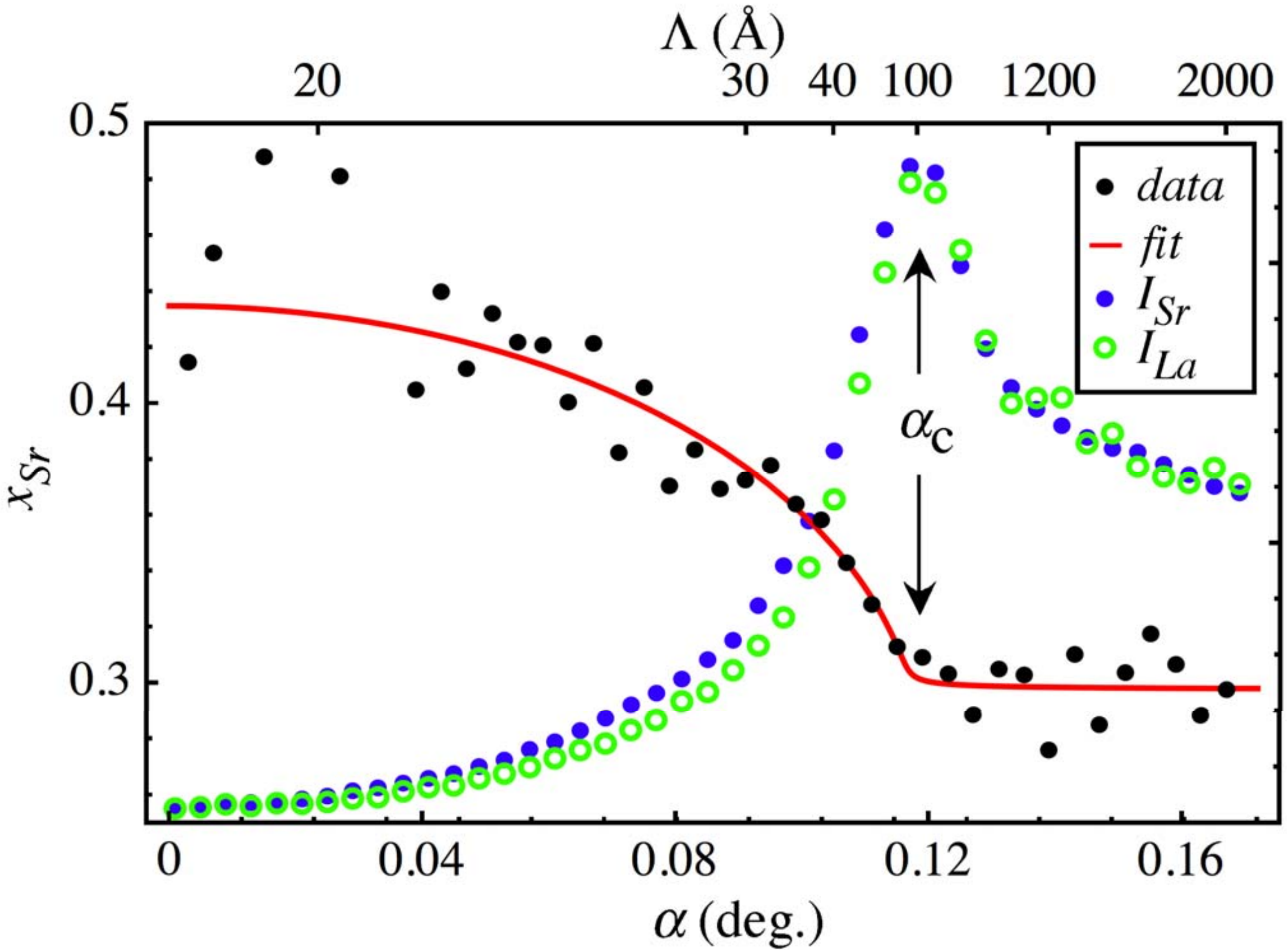
# *Total Reflection X-Ray Fluorescence (TXRF)*

**TXRF is a standard technique for analyzing impurities on semiconductor substrates since each element has a standard spectra.**

**We've extended it to quantitative studies of nanometer composition gradients at surfaces and buried interfaces.**



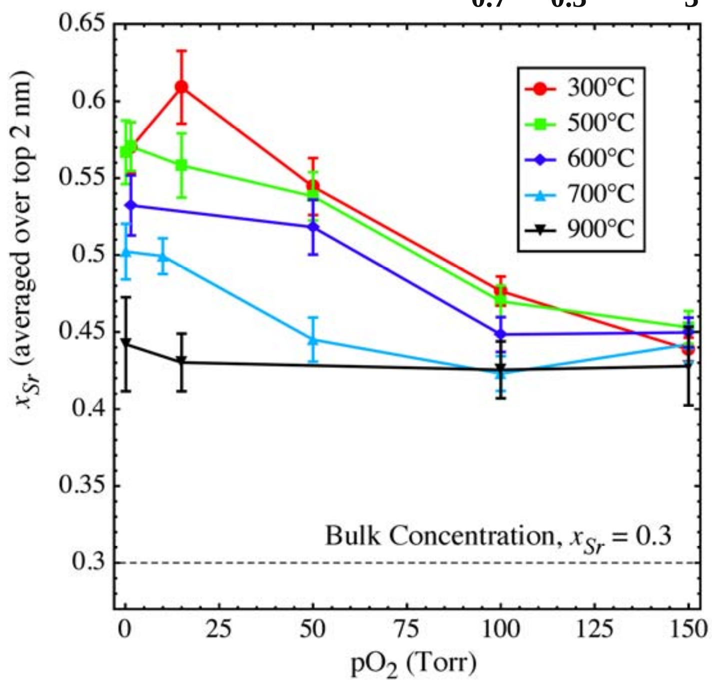
# Typical Analysis of TXRF



# $pO_2$ Dependence of Sr Surface Segregation

- **Observe that Sr segregation depends on both T and $pO_2$**
  - plot shows average Sr composition in ~3 nm surface region (bulk composition = 0.3)
- **Charged vacancies are often not considered in surface segregation studies. The concentration of these defects depends strongly on temperature *and* $pO_2$.**
- **A gradient of $V_O^{\bullet\bullet}$ near the surface could drive Sr segregation.**
  - Lowering $pO_2$ increases the concentration of $V_O^{\bullet\bullet}$ at the surface.
  - $V_O^{\bullet\bullet}$ have a net +2 charge; substituting Sr for La results in net -1 charge
  - Segregation of strontium ions can provide necessary charge compensation in the surface region.

**20 nm thickness $La_{0.7}Sr_{0.3}MnO_3$**




Change in Sr concentration from bulk

| | Operating T (700-1000 C) | Low T (300 C) |
|---|---|---|
| Low $pO_2$ (mTorr) | +35% | +50% |
| Operating $pO_2$ (atmospheric) | +21% | +25% |

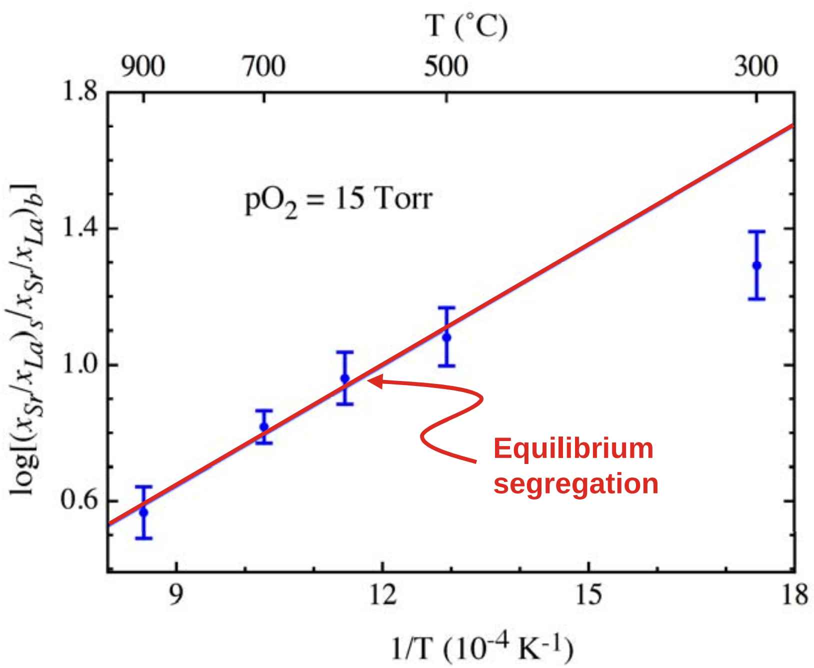
# Equilibrium vs. Non-Equilibrium Segregation

- Equilibrium segregation is typically analyzed by minimizing the free energy with respect to the solute concentration.
- Using TXRF data taken for $La_{0.7}Sr_{0.3}MnO_3$ on $DyScO_3$, we have fit the high temperature Sr/La ratios to obtain surface concentrations that can be used to extract (15 Torr $p(O_2)$)

  **$\Delta H_{seg}$ = -9.5 kJ/mol**

  **$\Delta S_{seg}$ = 0.38 J/K/mol**

- Linearity at high T (above 500˚C) indicates equilibrium segregation.
- Fall off at lower temperature results from the slow kinetics, e.g. non-equilibrium segregation.



# *In Situ Synchrotron Studies*

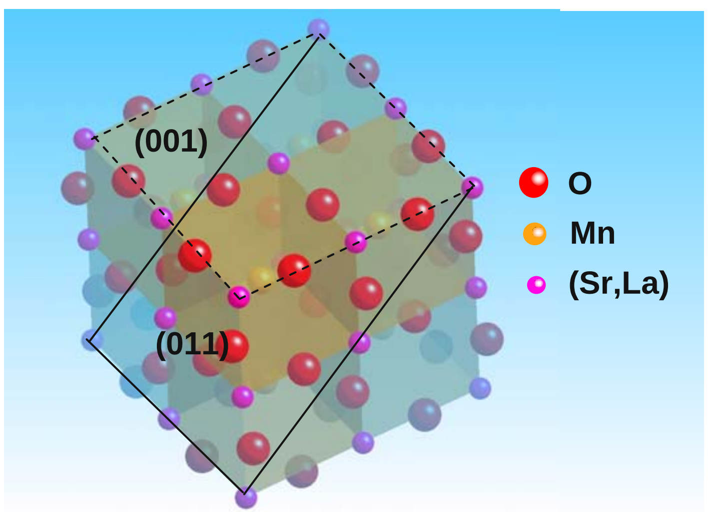
**In situ studies employ synchrotron x-ray scattering and spectroscopy tools. These techniques probe atomic-scale processes under SOFC operating conditions.**

- **In Situ Controlled Atmosphere Studies**
- **In Situ Electrochemical Studies**
  - Determine dynamic changes of cathode occurring in SOFC half-cell
  - Correlate with equilibrium structures and ex situ measurements
  - Films grown on YSZ as an electrolyte
- **In Situ Studies of Operating Fuel Cells**

# *LSM and LSC on YSZ(111)*

- Growth on YSZ(111) promotes LSM(011) and LSC(011) rather than (001) crystal orientation.
- Crystal orientation changes the degree of epitaxy and surface polarity.

**LSM Pseudocubic Unit Cell**




$La_{0.7}Sr_{0.3}MnO_3$ (001)

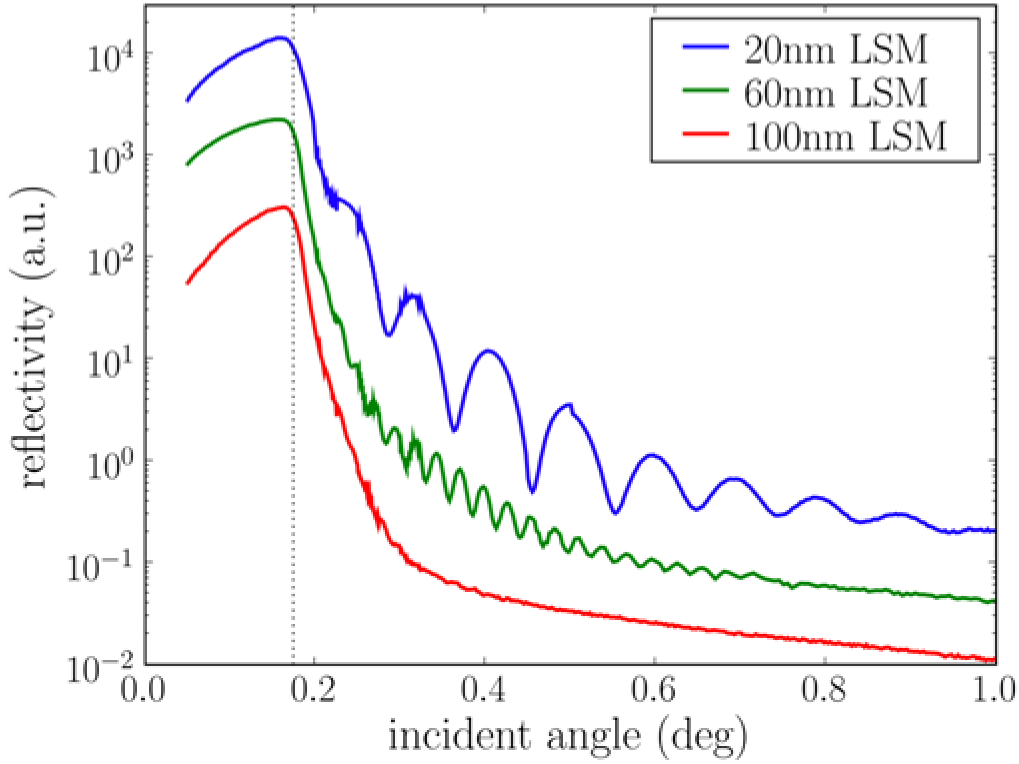
$La_{0.7}Sr_{0.3}O^{(+0.7)}$
$MnO_2^{(-0.7)}$
$La_{0.7}Sr_{0.3}O^{(+0.7)}$
$MnO_2^{(-0.7)}$

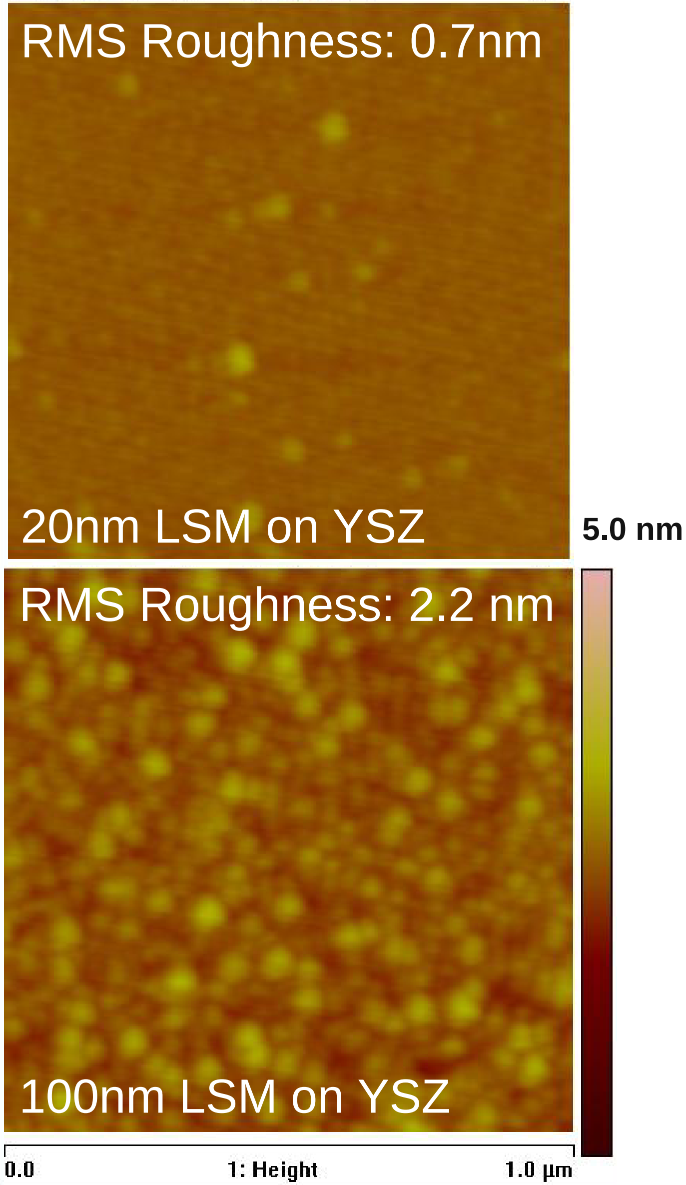
$La_{0.7}Sr_{0.3}MnO_3$ (011)

$La_{0.7}Sr_{0.3}MnO^{(+4)}$
$O_2^{(-4)}$
$La_{0.7}Sr_{0.3}MnO^{(+4)}$
$O_2^{(-4)}$

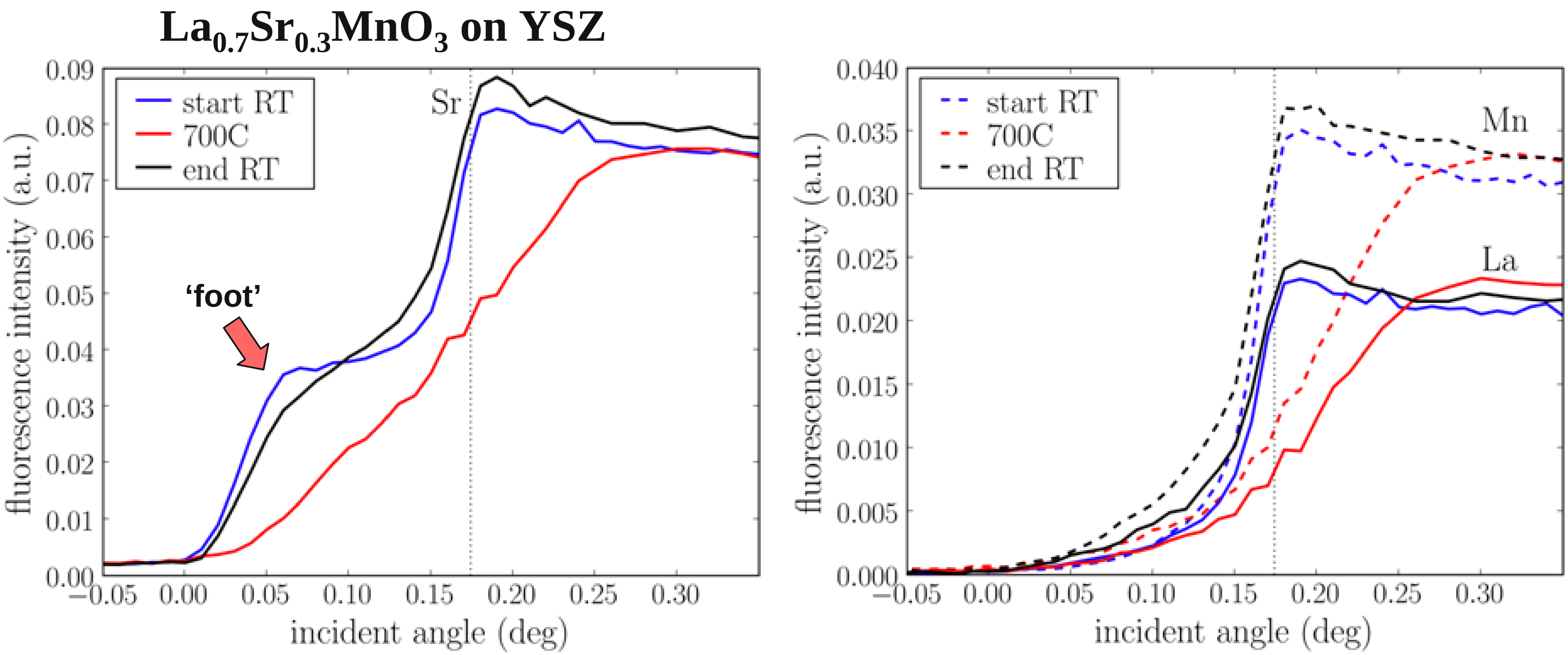
# Roughness of LSM (110) on YSZ (111)

- Atomic Force Microscopy of 'as-received' samples shows increasing roughness with film thickness
- X-Ray reflectivity shows well defined fringes for thin sample and no fringes for thick sample due to the increased roughness



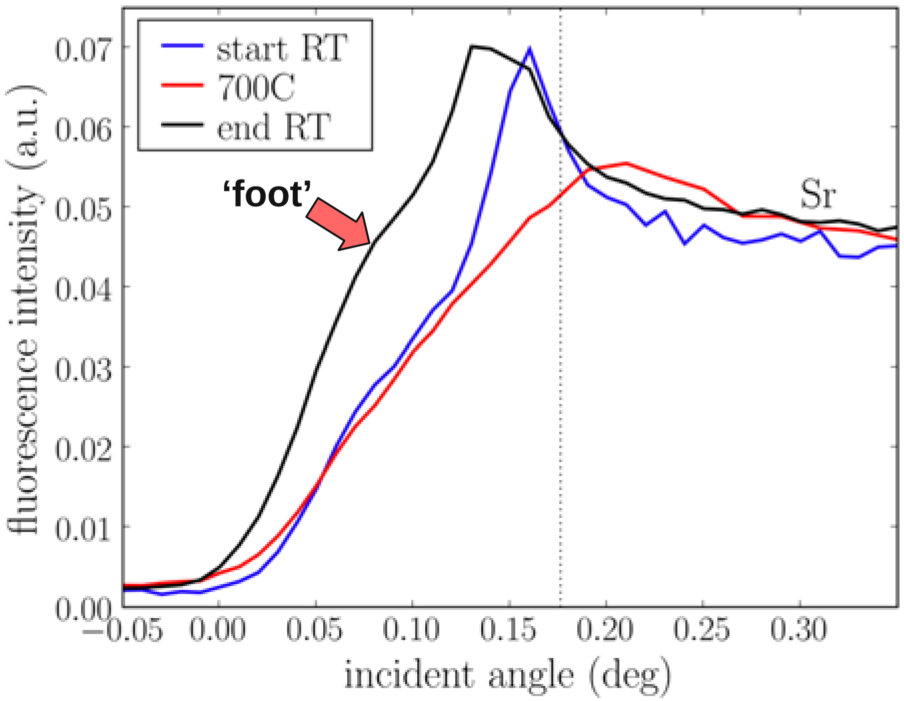
# Temperature Dependent TXRF of LSM(110)

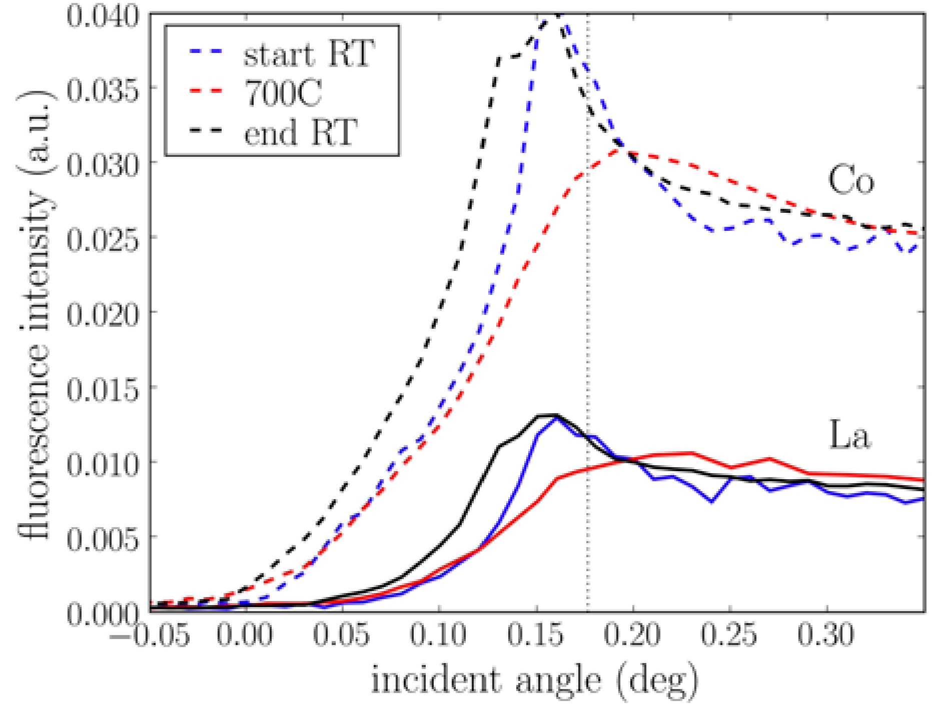



- At room temperature, there is a 'foot' in the Sr fluorescence but not in Mn and La.
- This is evidence of Sr rich particles at the LSM surface due to Sr segregation.
- This 'foot' gradually disappears at high temperature implying particles are re-incorporated.
- Process is reversible, 'foot' reappears (Black line) at room temperature even after rapid cooling (700°C to room temperature in 30 minutes).

# Temperature Dependent TXRF of LSC(110)

**$La_{0.7}Sr_{0.3}CoO_3$ on YSZ**



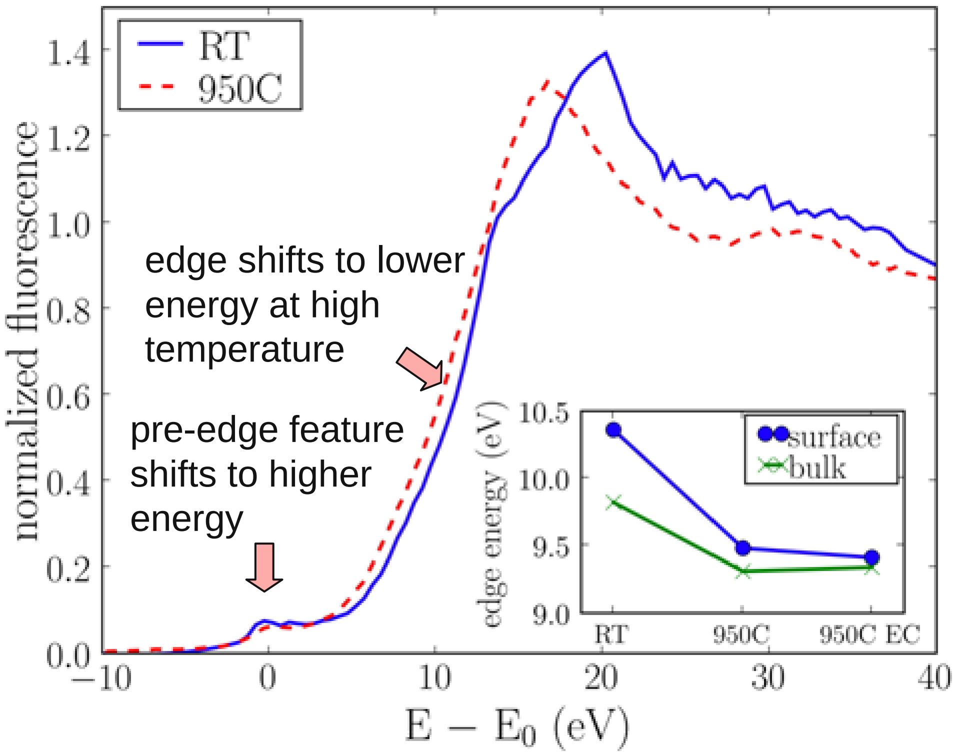

- At room temperature, only a faint sign of 'foot' in Sr fluorescence.
- Sr segregation is much less than LSM.
- Sr segregation is enhanced (Black line) when cooling down to room temperature after cathodic and anodic polarizations (±100 mV for 1 hr each) at 700C.

# *Co K edge XANES of LSC(110)*

**X-Ray Absorption Near-Edge Structure (XANES) is sensitive to the chemical state of the probed atom**

- Surface and bulk XANES taken (only surface XANES are shown).
- The position of the Co K edge shows the average Co oxidation state (higher oxidation state: higher energy).
- Changes in Co XANES are indicative of increase in $V_O^{\bullet\bullet}$ concentration at higher temperature.

**$La_{0.7}Sr_{0.3}CoO_3$ on YSZ**



# *Summary of in situ Electrochemistry Data*

| sample | cooling to room temperature | heating to high temperature | electrochemistry |
|---|---|---|---|
| LSM | form Sr enriched particles at surface (Sr segregation) | Sr incorporation into film | may influence Sr segregation* |
| LSC | same as LSM but smaller effect | same trend as LSM. increase $V_O^{\bullet\bullet}$ (Co XANES) | may influence Sr segregation has no effect on Co oxidation state (Co XANES)* |

* **Preliminary results: Need further studies.**

# *Experimental Summary*

- **Controlled Atmosphere Experiments**
  - Sr surface segregation in LSM is observed at all temperature and $pO_2$ conditions
  - The dependence of Sr surface segregation is consistent with a charge neutralization mechanism for both oxygen vacancies and the polar LSM surface
- **Electrochemical Experiments**
  - Strong indication of Sr segregation at room temperature in LSM.
  - Sr segregation goes down at high temperature and goes up at room temperature even after fast cooling (700°C to RT in 30 min).
  - Changes in Co K edge XANES in LSC with heating but no significant change by electrochemistry.
  - Cathodic or anodic polarizations may control the Sr segregation and desegregation rates.
  - Full-cell experimental design in development.

# Synchrotron Studies - Next Steps

- **Develop structural models that can quantitatively explain the diffraction results (CTR and reflectivity)**
  - Can oxygen defect thermodynamics be quantitatively determined through these measurements?
- **Look at the chemical state of the B site atoms**
- **Incorporate flexible in situ electrical measurements into the controlled environment chamber**
- **Explore use of inelastic x-ray scattering to probe oxygen sites**
  - similar to XANES and EXAFS but information is coded on a high energy x-ray beam allowing penetration through complex samples

# *In Situ Synchrotron Studies*

**In situ studies employ synchrotron x-ray scattering and spectroscopy tools. These techniques probe atomic-scale processes under SOFC operating conditions.**

- **In Situ Controlled Atmosphere Studies**
- **In Situ Electrochemical Studies**
- **In Situ Studies of Operating Fuel Cells**
  - Focus on cathode side of fuel cell
  - Examine atomic structure and chemical state of individual constituents
  - Correlate with ex situ measurements and performance data

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