Creation, Understanding, and Control of Functional Oxide Heterostructures

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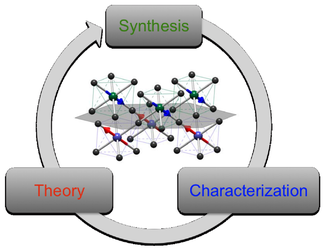
X-ray Science Division

Abstract: Emergent behavior that arises from competing interactions within a system, offer unique pathways to the creation of materials with novel functionalities. While this offers a pathway to applications in energy science, much of the physical framework is still poorly understood. Oxide heterostructures offer opportunities beyond single phase materials to mix properties within artificial structures to create wholly new phases. However, without deep understanding, the rational design of these materials will remain difficult. Here we highlight the power of X-ray tools which are creating the insight needed to create a future energy materials paradigm.

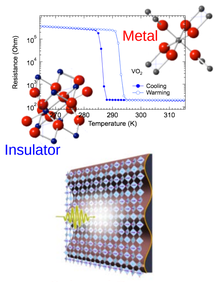
Overview

Coupling advanced X-ray probes with in-situ capabilities for rapid creation of novel materials with enhanced functionality

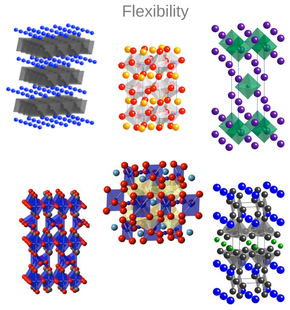


Functional Complex Oxides

Emergent Behavior

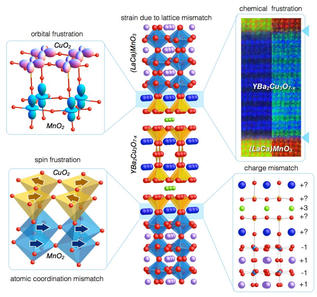


Structural and Chemical Flexibility



New Materials via Interfaces

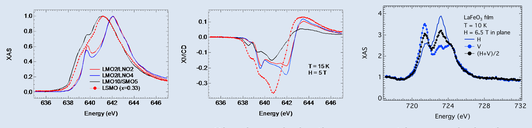
Understanding how to balance competing degrees of freedom at interfaces



X-ray Tools

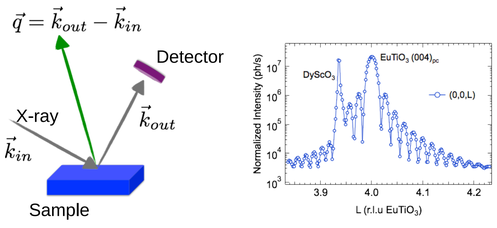
Polarized spectroscopies provides element-resolved information about:

Valence | Magnetic moment | Orbitals & Antiferromagnetism



Circular polarization | Linear polarization

X-ray diffraction from lattice planes informs about structure



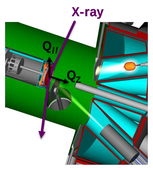
At absorption resonance can also be sensitive to complex order (charge, orbit, spin)

These tools can also be explored in spatially and temporally resolved modes

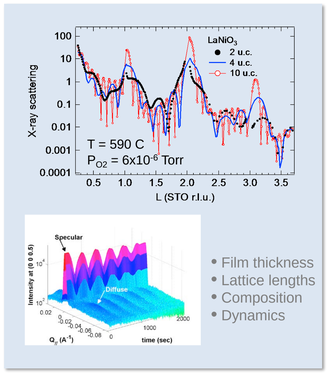
Creation

In-situ Synthesis

X-rays provide quantitative information!



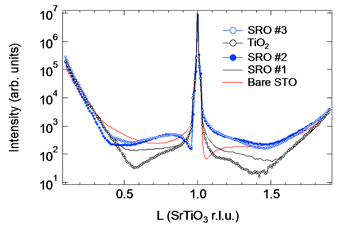
Oxide MBE (33-ID)

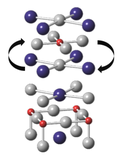


- Film thickness
- Lattice lengths
- Composition
- Dynamics

Dynamic Layer Swapping

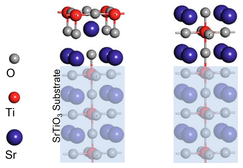
Understand layer by layer formation of crystalline phases with oxide MBE





Layers dynamically rearrange during growth

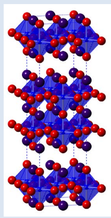
Theoretical energetics favor layer swapping

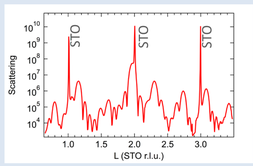


DFT: 0 eV
EP: 0 eV

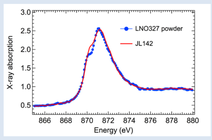
DFT: -0.63 eV
EP: -0.54 eV

Layer swapping to create new materials





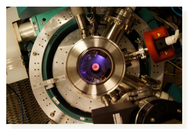
Created by non-standard vision generated by theoretical understanding of reconstruction during growth



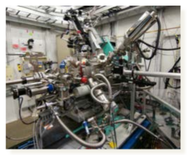
In collaboration with D.D. Fong (MSD), J. Jellinek (CSE), and D. Morgan (UW Madison)

Other Oxide Film Growth Modes

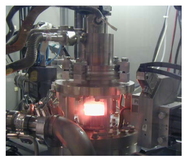
Off-axis sputtering (12-ID)



Pulsed Laser Deposition (33-ID)



MOCVD(12-ID)



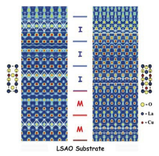
Atomic Layer Deposition (12-ID)

Understanding

Structure

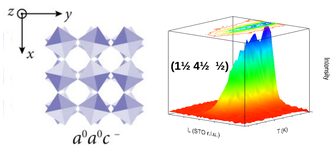
X-ray diffraction offers detailed insight to oxide films

Structure (COBRA)

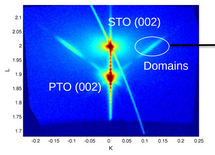


H. Zhou et al. PNAS **107**, 8103 (2010)

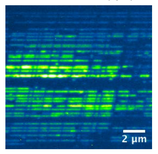
Octahedral rotations and symmetry



3D Reciprocal Space Mapping



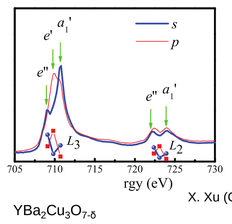
Diffraction Microscopy (XRIM)



In collaboration with N. Laanait, D.D. Fong, and P. Fenter (ANL)

Electronic

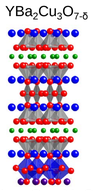
Polarized spectroscopies detailed element-resolved valence and orbital configurations



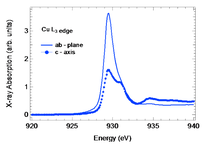
Quantitative exploration of the effect of chemical coordination

X. Xu (ORNL) et al. Appl. Phys. Lett. **101**, 241907 (2012)

$YBa_2Cu_3O_{7-\delta}$



$La_{2/3}Ca_{1/3}MnO_3$

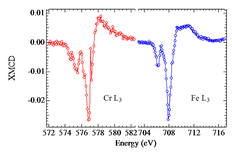


Microscopic details of orbital configurations

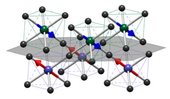
In collaboration with J. Chakhalian (Univ. of Arkansas)

Magnetic

Element resolved magnetism at oxide interfaces

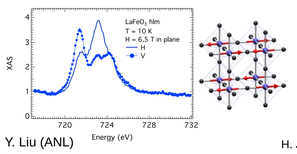


Designing new ferromagnetic insulators



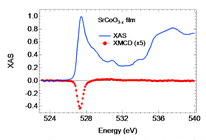
B. Gray et al. Appl. Phys. Lett. **97**, 13105 (2010)

Antiferromagnetism in ultrathin films



Y. Liu (ANL)

Polarized oxygen states



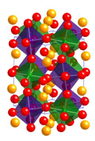
H. Jeen et al. Nature Materials **12**, 1057 (2013)

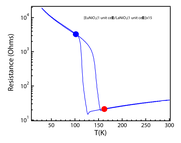
Ordered Phases

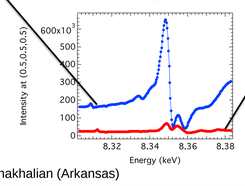
Resonant scattering to probe complex ordered phases

Tuning charge order in $RNiO_3$ superlattices

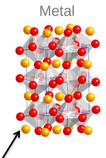
Insulator







Metal



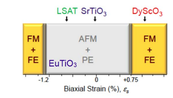
Resonant signal tied to inter-site electronic contrast

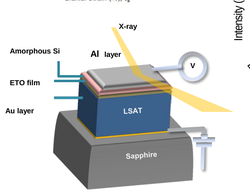
D. Meyers, J. Chakhalian (Arkansas)

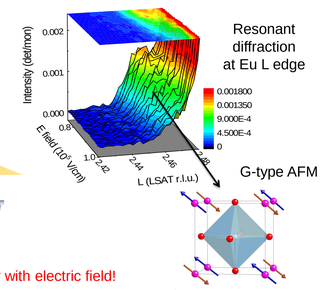
Control

Field Control

Explore connection between electric polarization and magnetism in strained $EuTiO_3$







Direct control of AFM order with electric field!

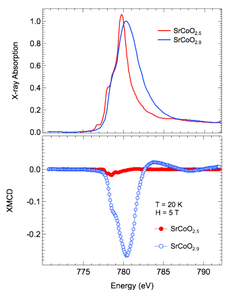
P.J. Ryan, J.W. Kim, et al. Nat. Commun. 4, 1334 (2013)

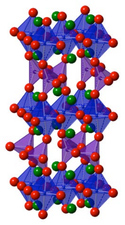
Vacancy Control

Reversible thermal control of oxygen content controls material properties

$SrCoO_3$

Cubic
Metallic
Ferromagnetic





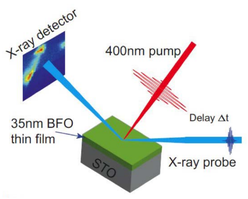
$SrCoO_{2.5}$

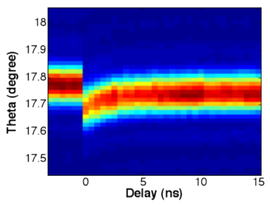
Brownmillerite
Insulating
Antiferromagnet

Electrochemical methods allow direct non-thermal control of vacancies

Optical Control

Track structure with time-resolved x-ray diffraction



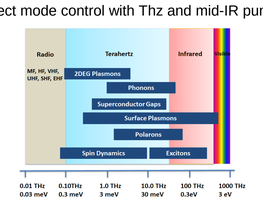


Dynamic strain in $BiFeO_3$ film due to long lived electronic carriers

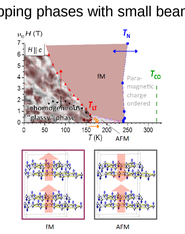
H. Wen et al. Phys. Rev. Lett. **110**, 37601 (2013)

Future Opportunities

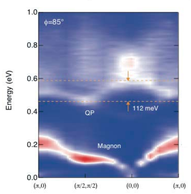
Direct mode control with Thz and mid-IR pumping

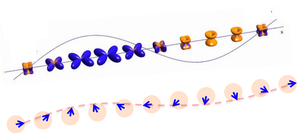


Mapping phases with small beams



Probing novel excited phases with RIXS





Jungho Kim, et. al., PRL. **108**,177003 (2012).