Quantitative Chemical Imaging of Atomic-Scale Chemistry Changes at Interfaces

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Purpose

- Develop a robust method to quantify atomic-scale changes in structure, composition, and bonding that occur at interfaces
- Make use of advanced capabilities for chemical imaging under varied environmental conditions afforded by the new generation of aberration-corrected microscopes and in situ stages

Expected Outcomes

- Apply methods to understanding interplay of structure-composition and properties at interfaces in functional oxides
- Use methods to increase throughput for materials analysis; focus on variance and similarities between materials systems
- Develop robust statistical methods for reproducible, quantified image analysis/interpretation

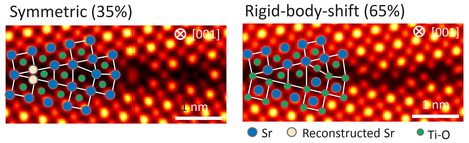
Key Successes

10 invited presentations at conferences and research institutions, 3 papers published

Research Accomplishments

Effect of Nonstoichiometry on Grain Boundary Energetics

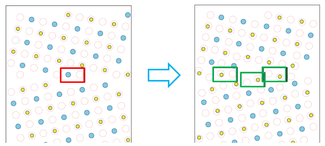
Symmetric (35%) Rigid-body-shift (65%)



Analyze many images to determine the statistical prevalence of a particular grain boundary plane

Density functional theory grain boundary simulations

Stoichiometric Model Ti-Excess Model



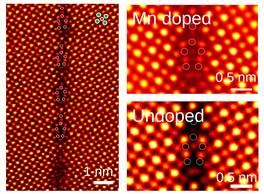
Yang H et al. 2013. *Philosophical Magazine* 93(10-12):1219-1229

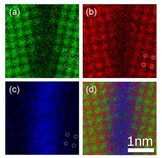
Atomic Structure	Statistical Population	Calculated GB Energy [J/m^2]
Symmetric	35%	0.98
Rigid-body-shift	65%	0.81

Nonstoichiometry plays an important role in determining grain boundary defect energetics

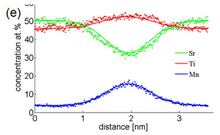
Effect of Impurity Doping on Grain Boundary Structures

Mn-doped $SrTiO_3$ grain boundary structure



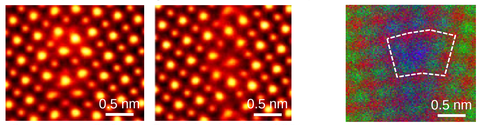


Atomic EDS mapping



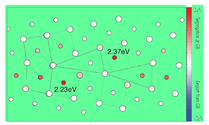
Mn at interstitial sites in the grain boundary, stabilizing the symmetric structure.

Pr-doped $SrTiO_3$ grain boundary structure



Symmetric 81% Rigid-body-shift 19% Atomic EDS

Pr Segregation Energy DFT calculation

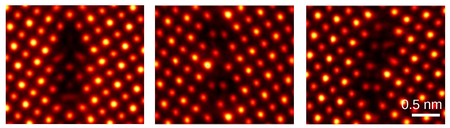


Yang H et al., in preparation

Pr preferentially segregates at two Ti sites.

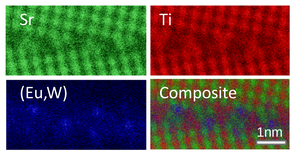
Statistical population inverted from the undoped grain boundary Pr stabilizes the symmetric structure.

Eu, W co-doped $SrTiO_3$ grain boundary structure



Symmetric Rigid-body-shift Low-symmetry

Atomic EDS



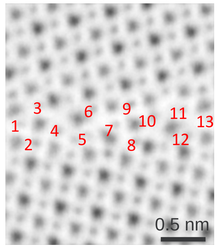
Co-doping induces a larger degree of structure variability.

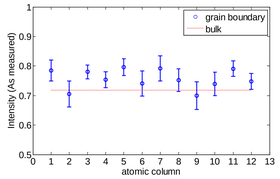
Yang H et al., in preparation.

Effect of Oxygen Vacancies

Direct visualization of oxygen vacancies

Annular Bright Field (ABF)

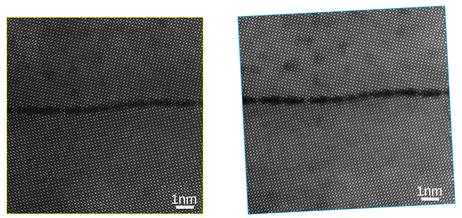




Yang H et al., in preparation.

Creation of oxygen vacancies

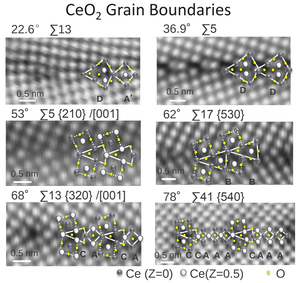
Slightly reduced in ETEM Further reduced in ETEM



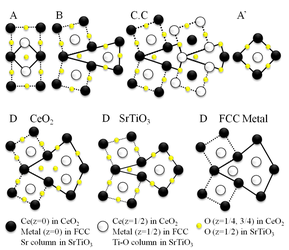
Formation of "dark contrast" during the creation of oxygen vacancies in ETEM

Generic Grain Boundary Structures

CeO_2 Grain Boundaries

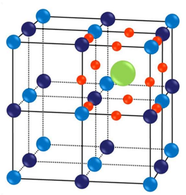


Generalized Structural Units



Symmetries in a broad band of dense packing cubic materials

Materials	Space Group	●	●	●	●
$SrTiO_3$	$Pm\bar{3}m$	Sr	O	Ti	Ti
ReO_3	$Pm\bar{3}m$	□	O	Re	Re
CeO_2	$Fm\bar{3}m$	O	□	Ce	□
Mg_2Sn	$Fm\bar{3}m$	Mg	□	Sn	□
MgO	$Fm\bar{3}m$	□	□	Mg	O
FCC	$Fm\bar{3}m$	□	□	metal	□



General models are originated from the similarities in crystallographic symmetry across a variety of materials systems.
Tong W et al. 2013. *Acta Materialia* 61(9):3285-3296.

Next Steps

- Understanding the defect dynamics of oxygen vacancies in grain boundaries through in situ environmental transmission electron microscopy (ETEM) experiments
- Direct visualization of oxygen vacancies though quantitative interpretation of ABF image contrast.
- Exploring structural similarity in dense packing cubics from different crystal orientations

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