Stanford University

Surface Properties of Substituted Lanthanum Ferrites under SOFC conditions

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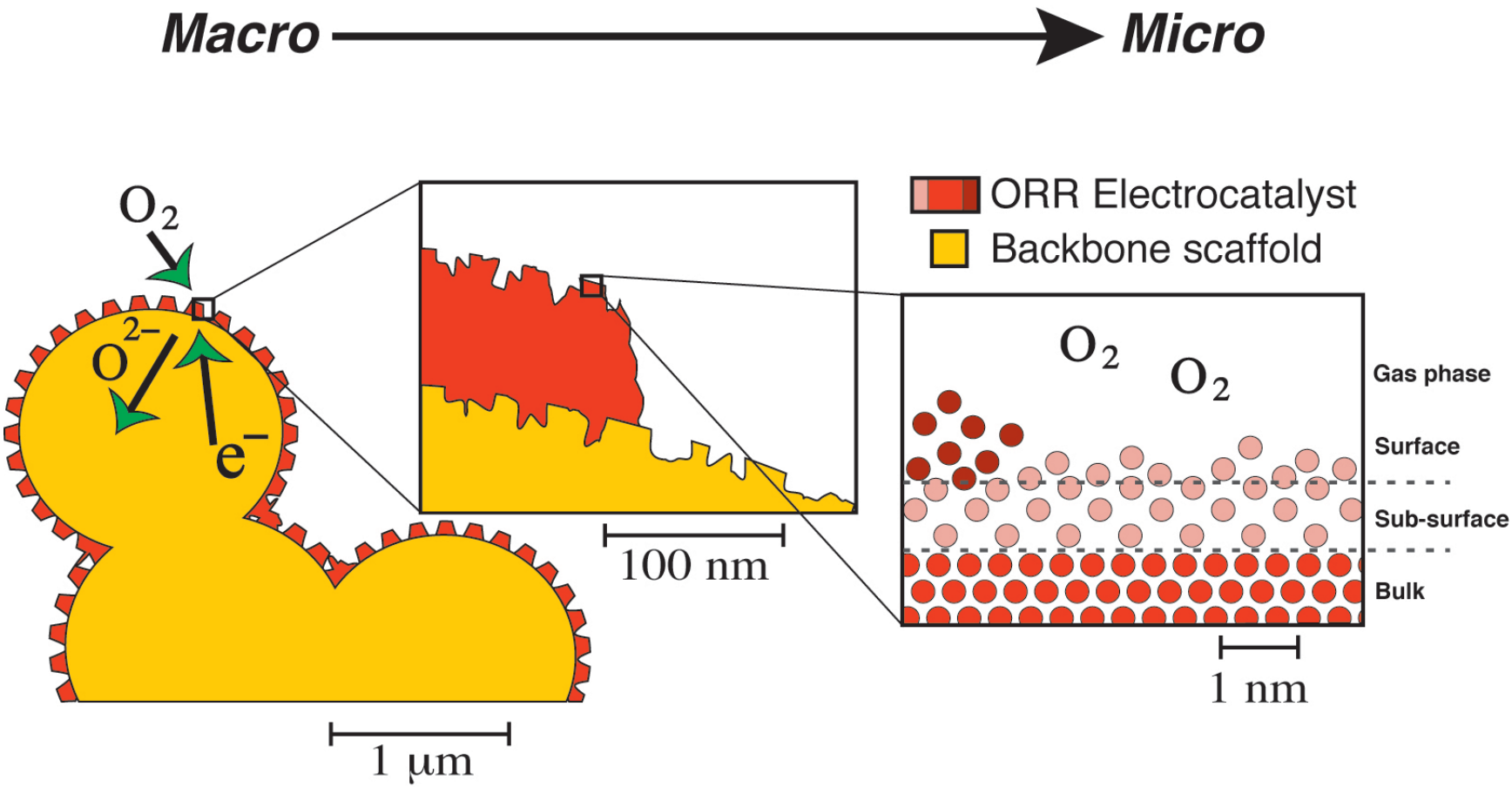
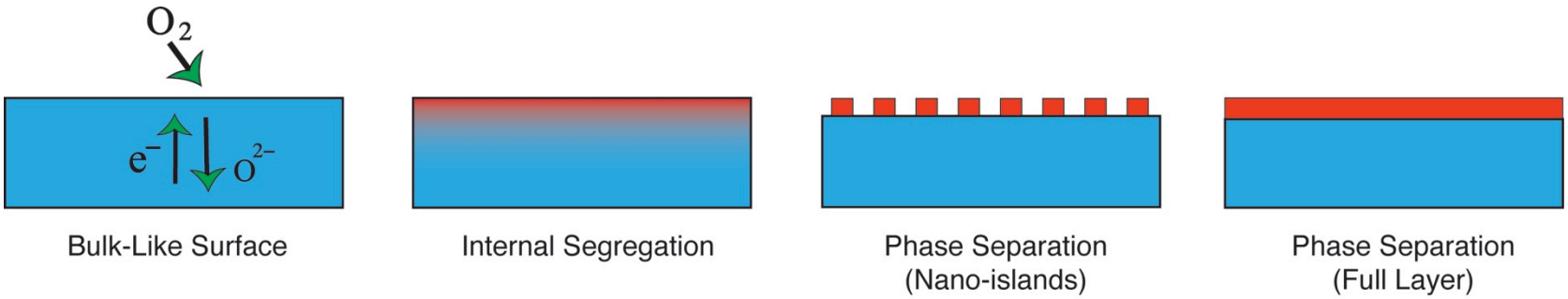
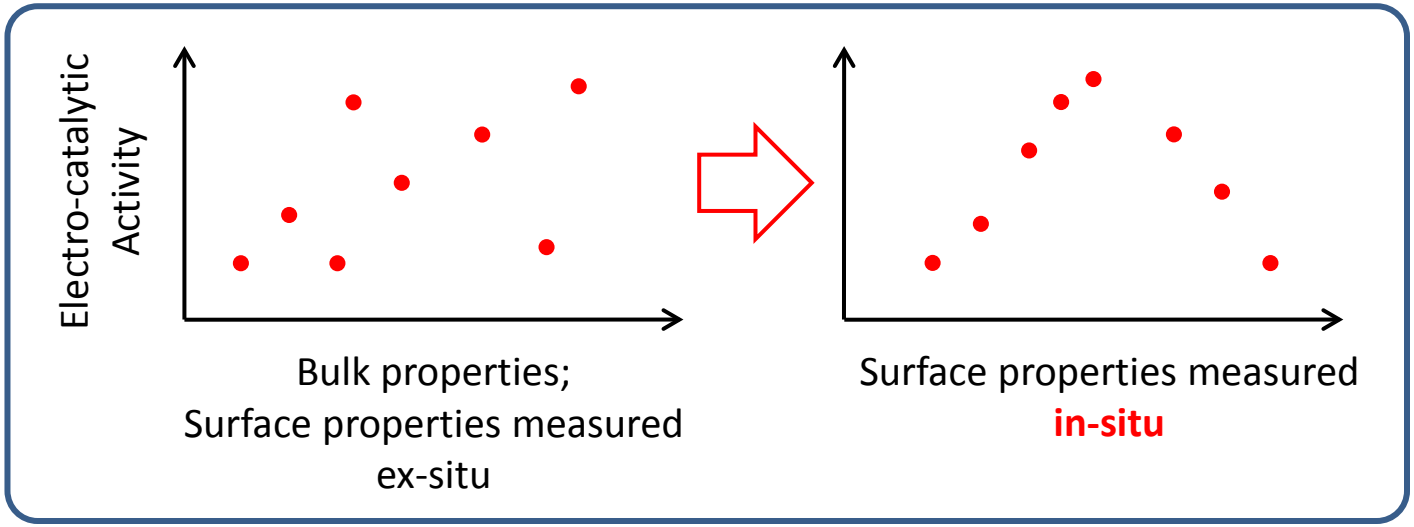


What's the nature of the active site?

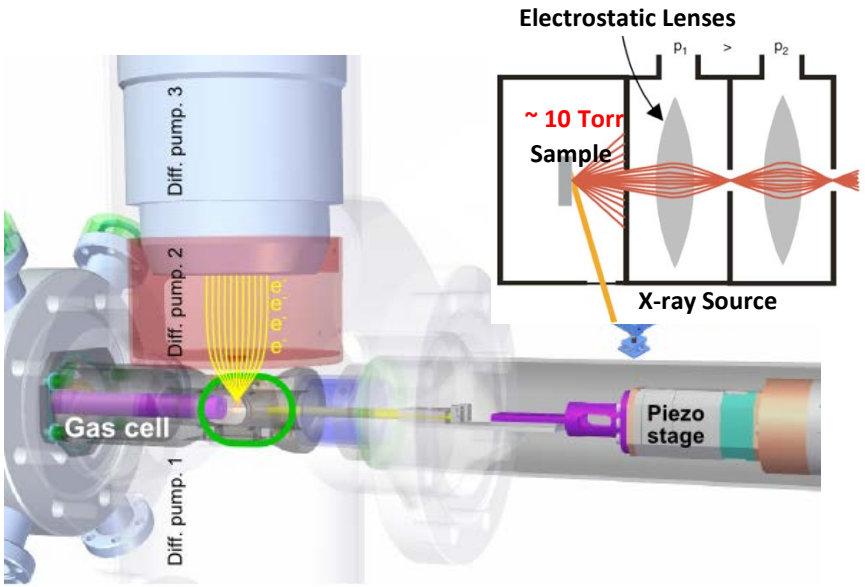
What controls ORR activity?



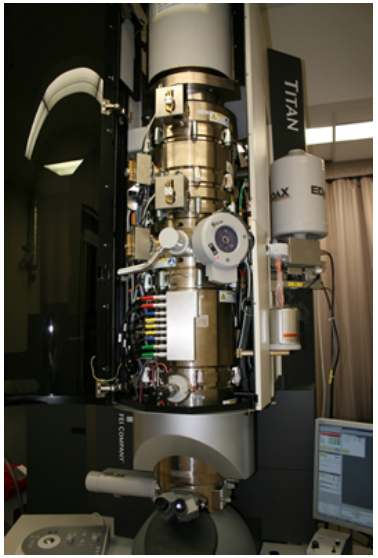


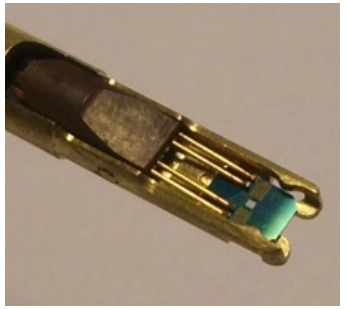
1. Identify the nanoscale active phase
2. Identify microscopic activity descriptors
3. Stabilize the active phase on (La,Sr)(Co,Fe)$O_{3-\delta}$

Ambient Pressure X-ray Spectroscopy

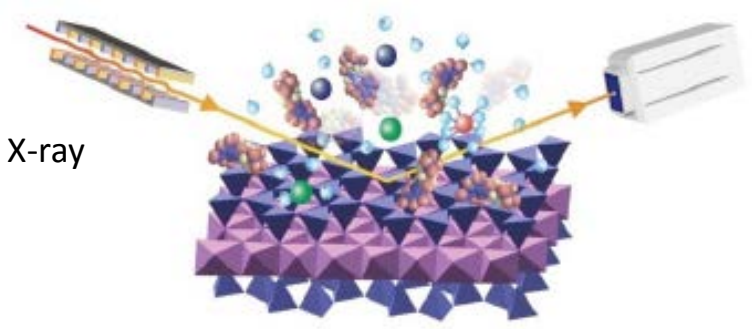


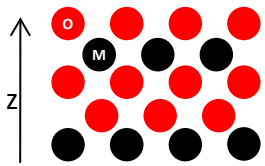
Environmental Transmission Electron Microscopy (TEM)



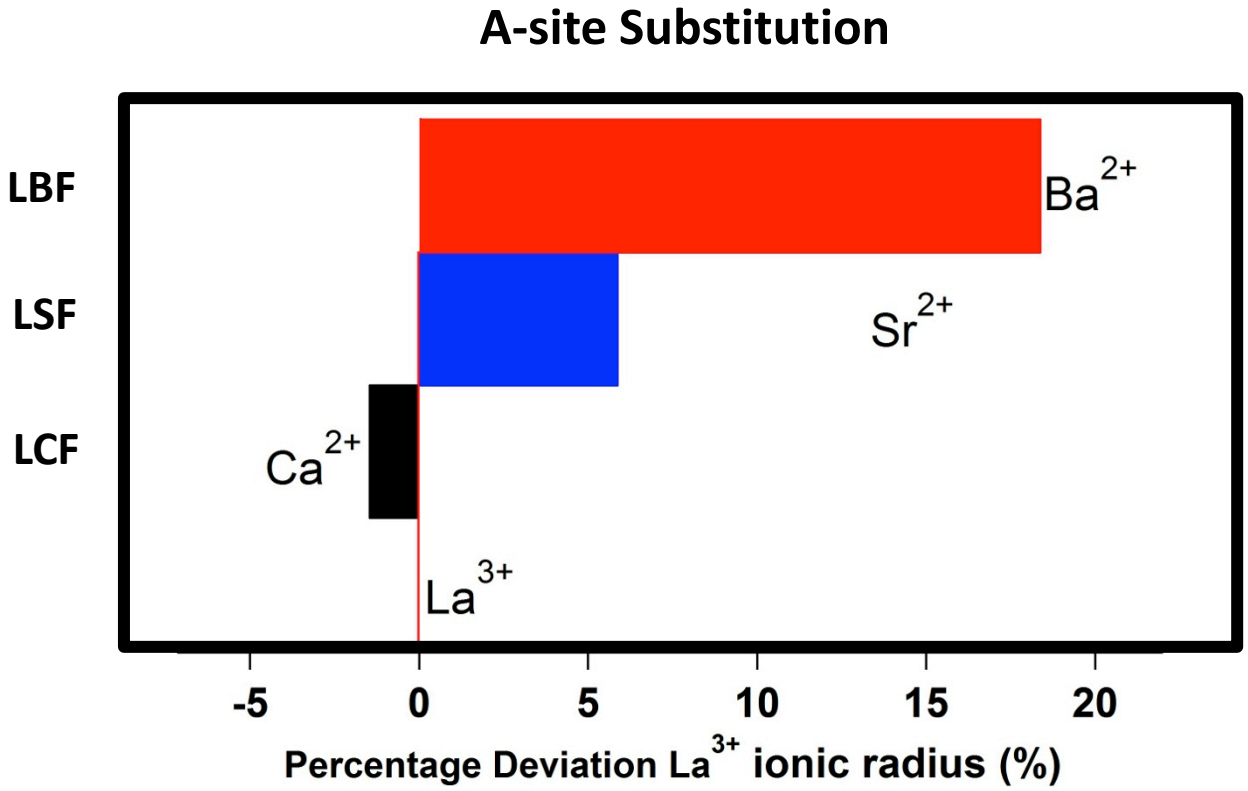


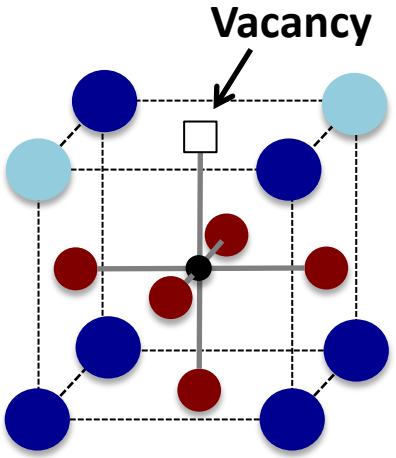
Surface X-ray Scattering





Size effect of Substitution Atom





$La_x(AE)_{1-x}FeO_{3-\delta}$

Shannon, Acta Cryst. (1976). A32, 751

Highlights

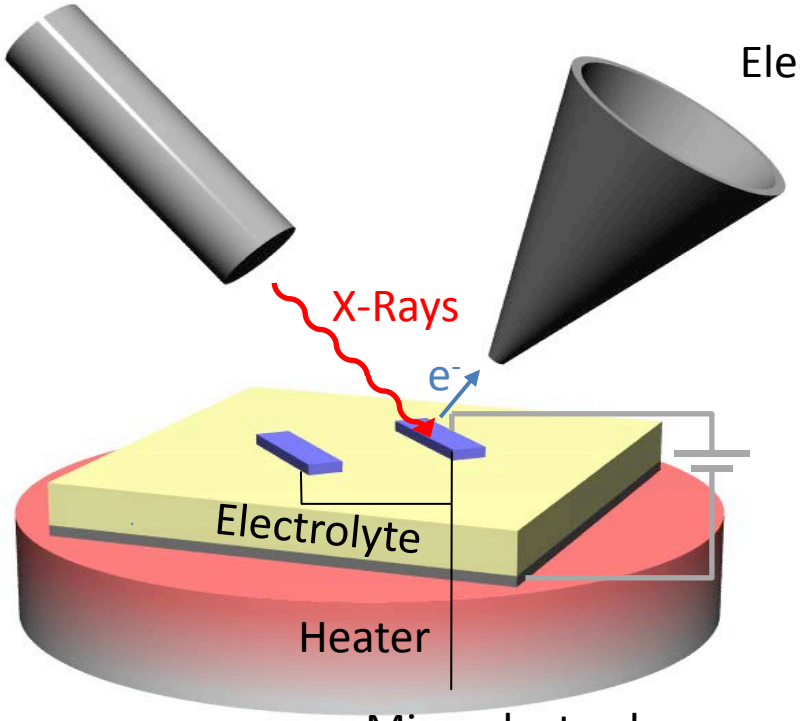
Ba/Sr substitution gives two surface phases, Ca- only one

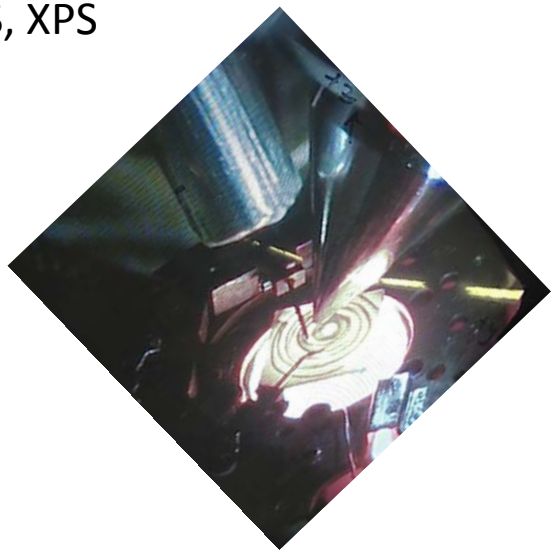
Ba segregates to the surface forming a new phase regardless of A/B site ratio

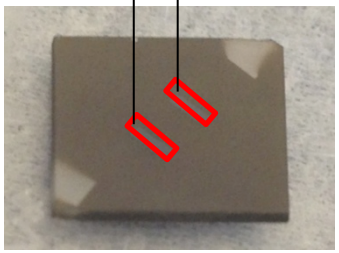
Small A/B site ratio changes in bulk can give significant composition variation on the exposed surface

Changing the oxygen chemical potential by electrochemically biasing affects Ba solubility

In operando Ambient Pressure X-ray Photoelectron Spectroscopy

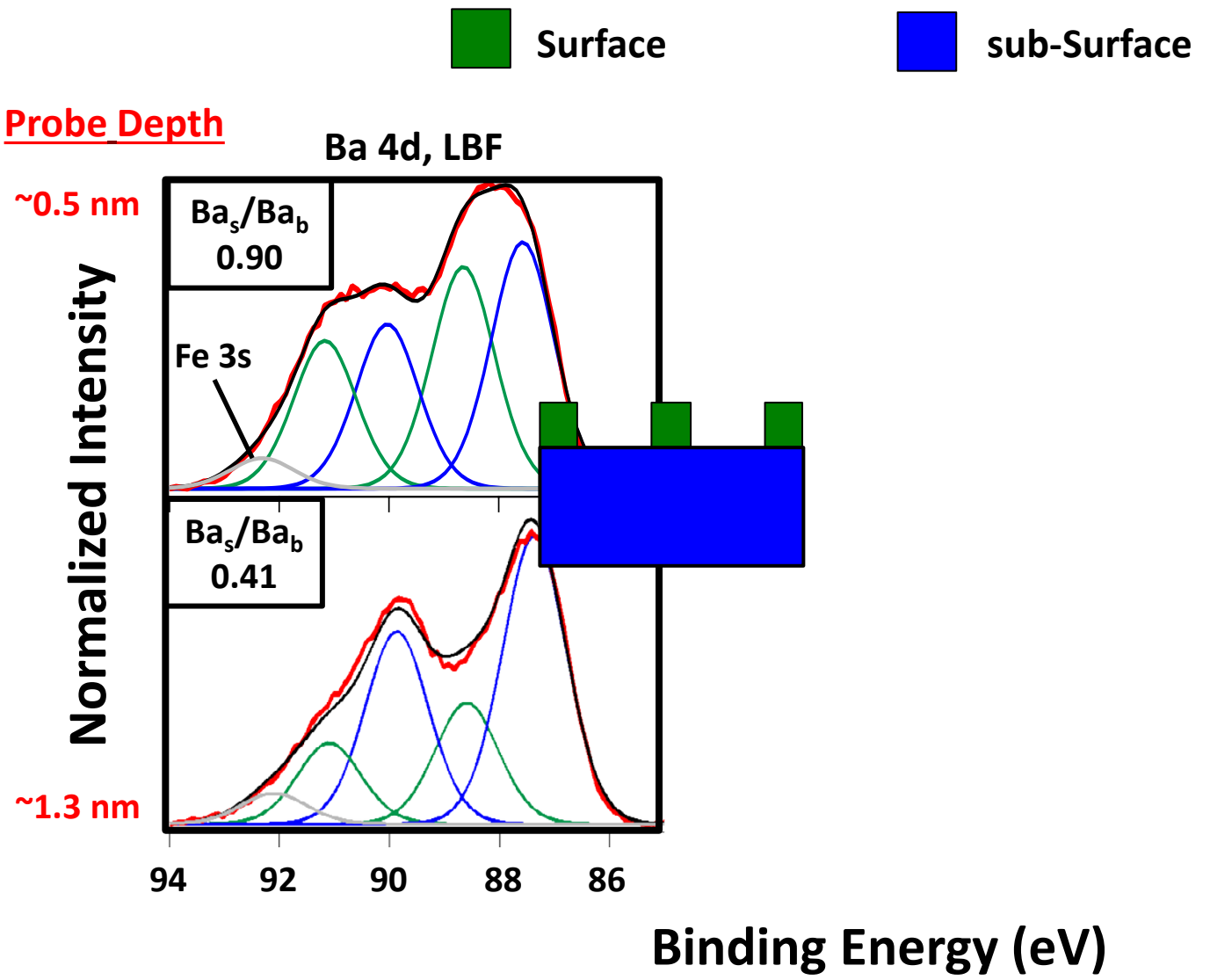






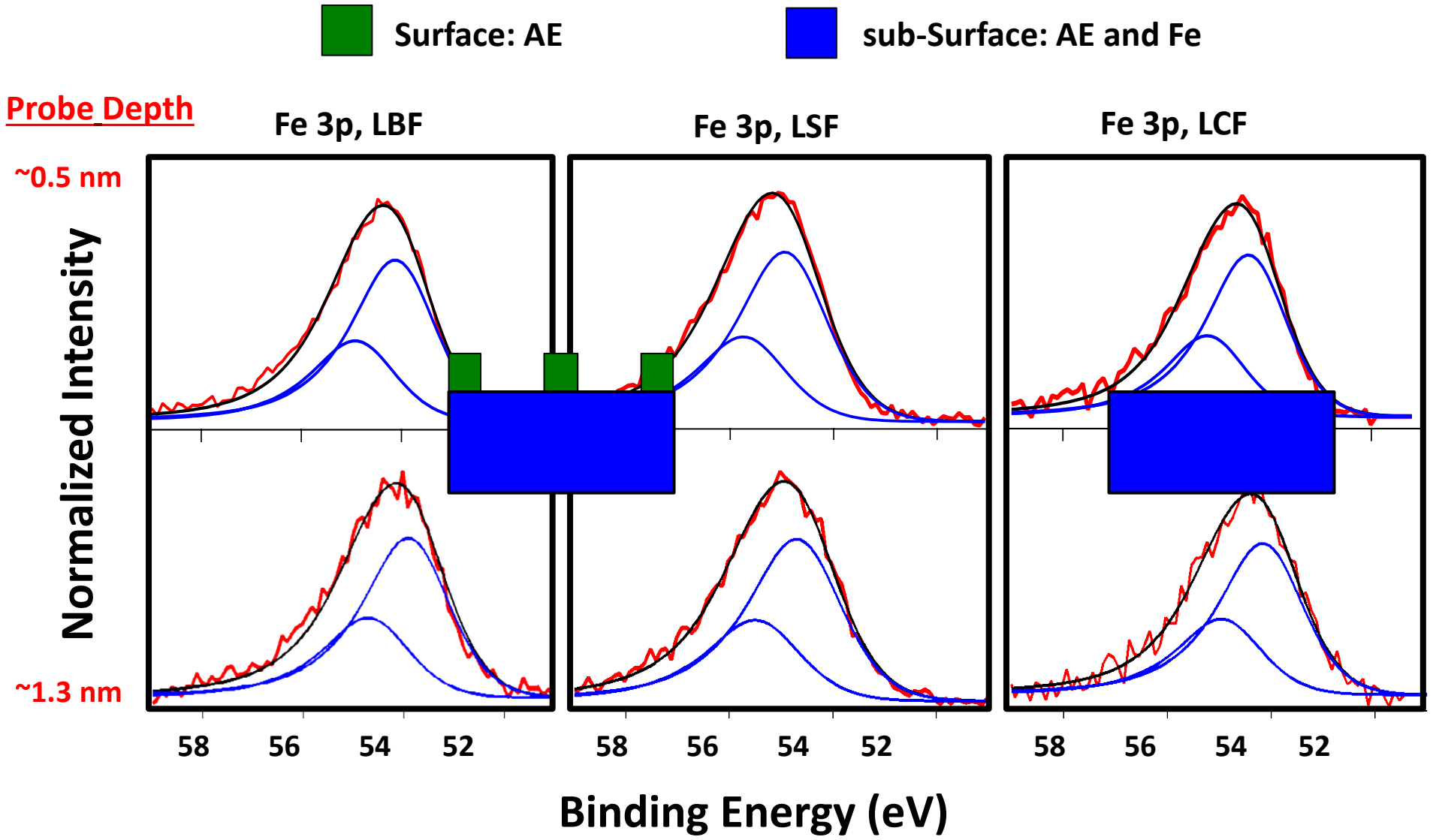
pO_2 = 1 Torr **T = ~470 °C**

Ca does not produce two phases



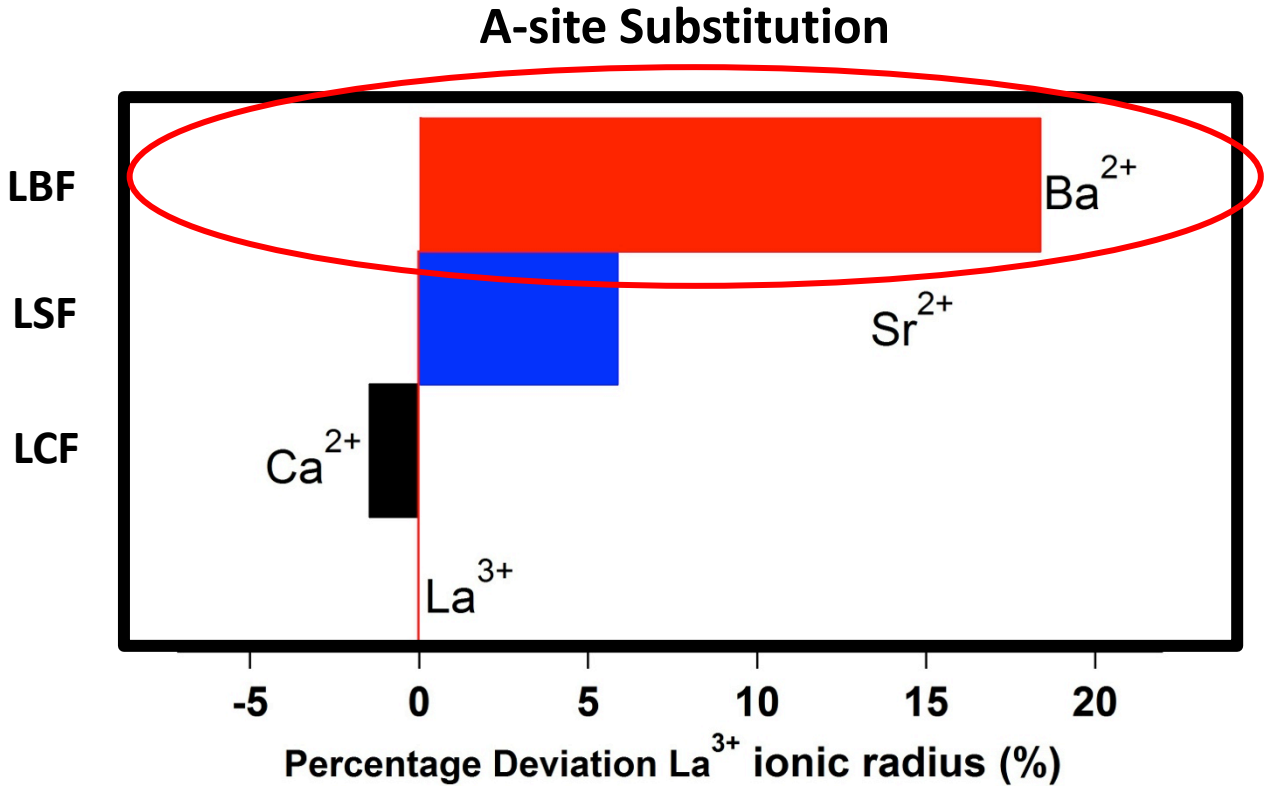
NIST 82 Database

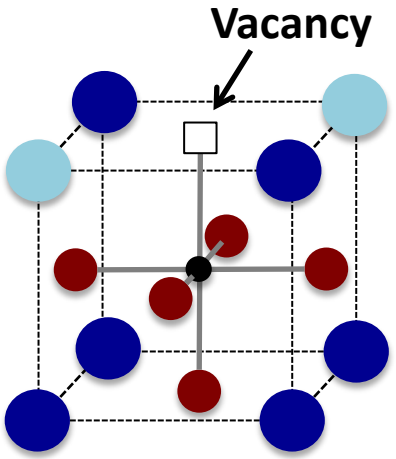
Fe signal is same for all substituents



NIST 82 Database

Size effect of Substitution Atom

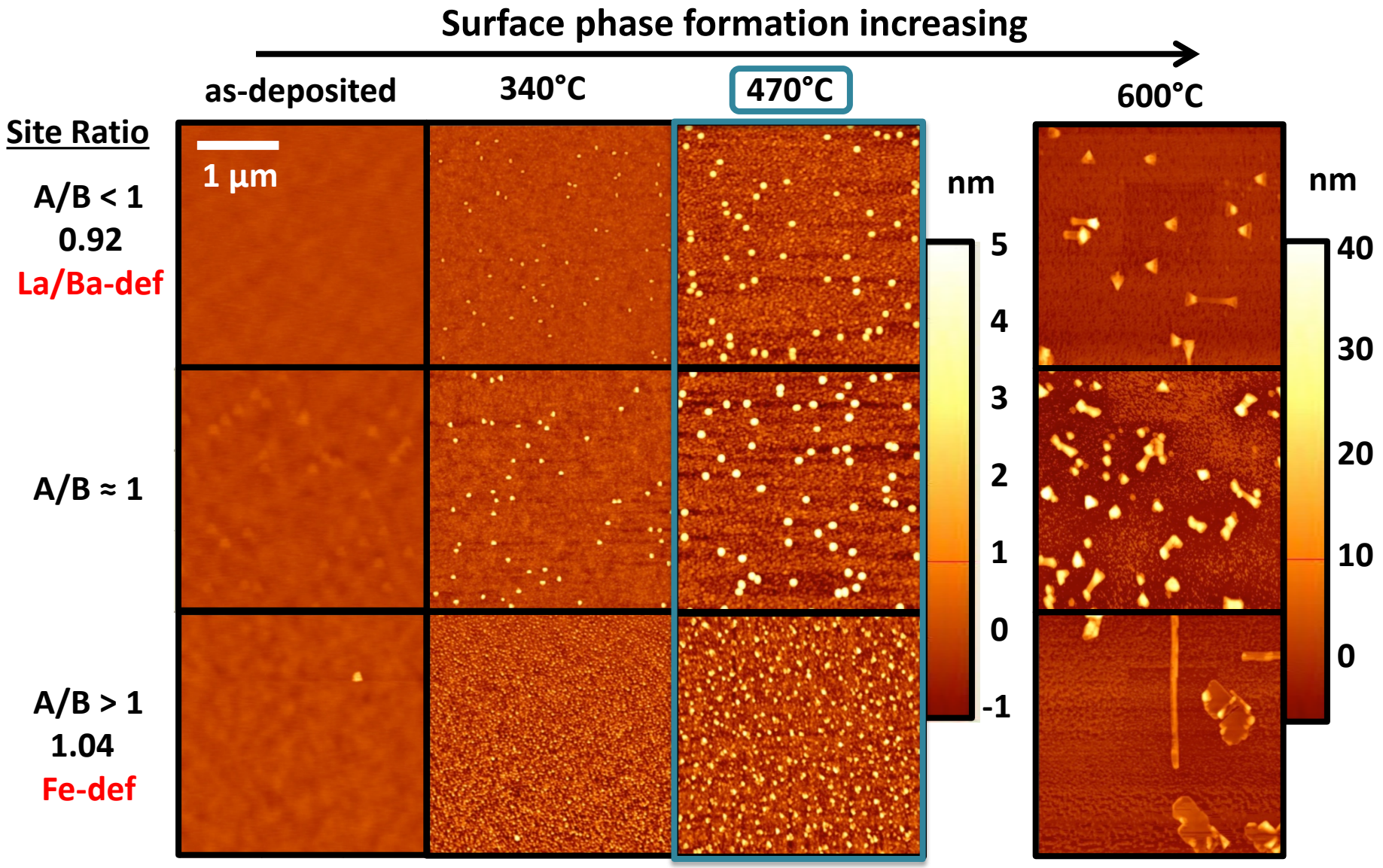




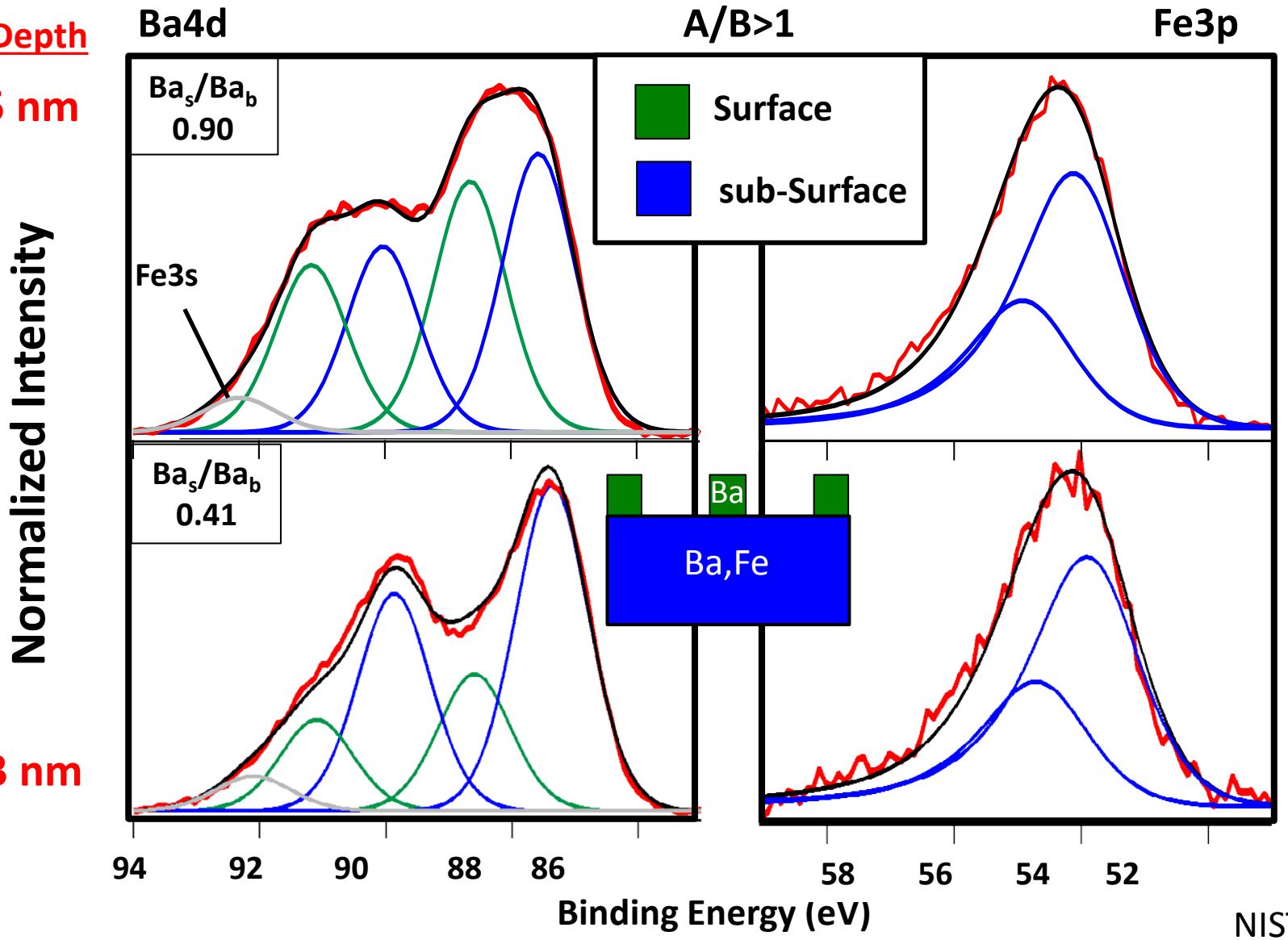
$La_x(AE)_{1-x}FeO_{3-\delta}$

Shannon, Acta Cryst. (1976). A32, 751

AFM of quenched samples : 1Torr O_2

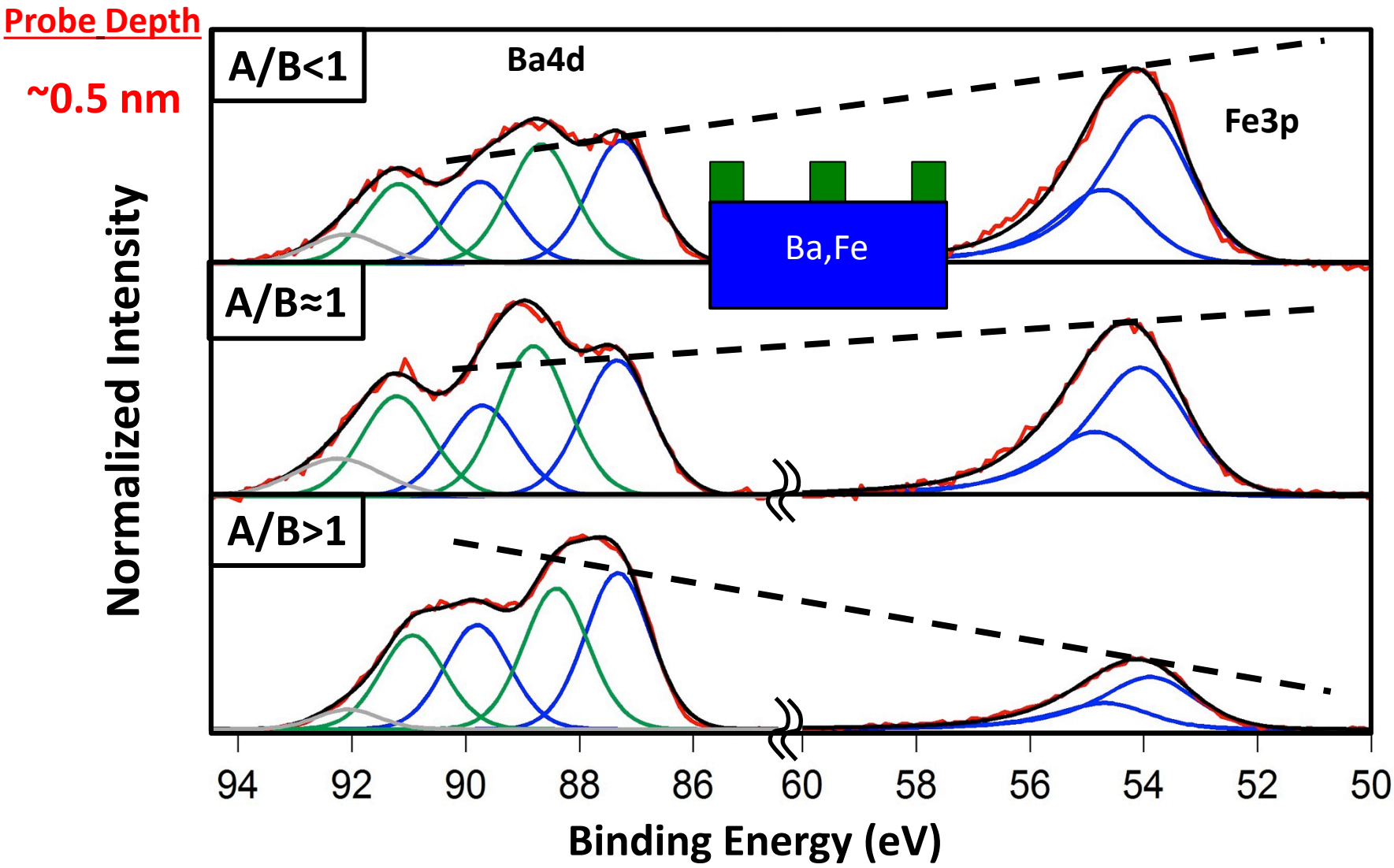


Ba4d signal changes but Fe3p same

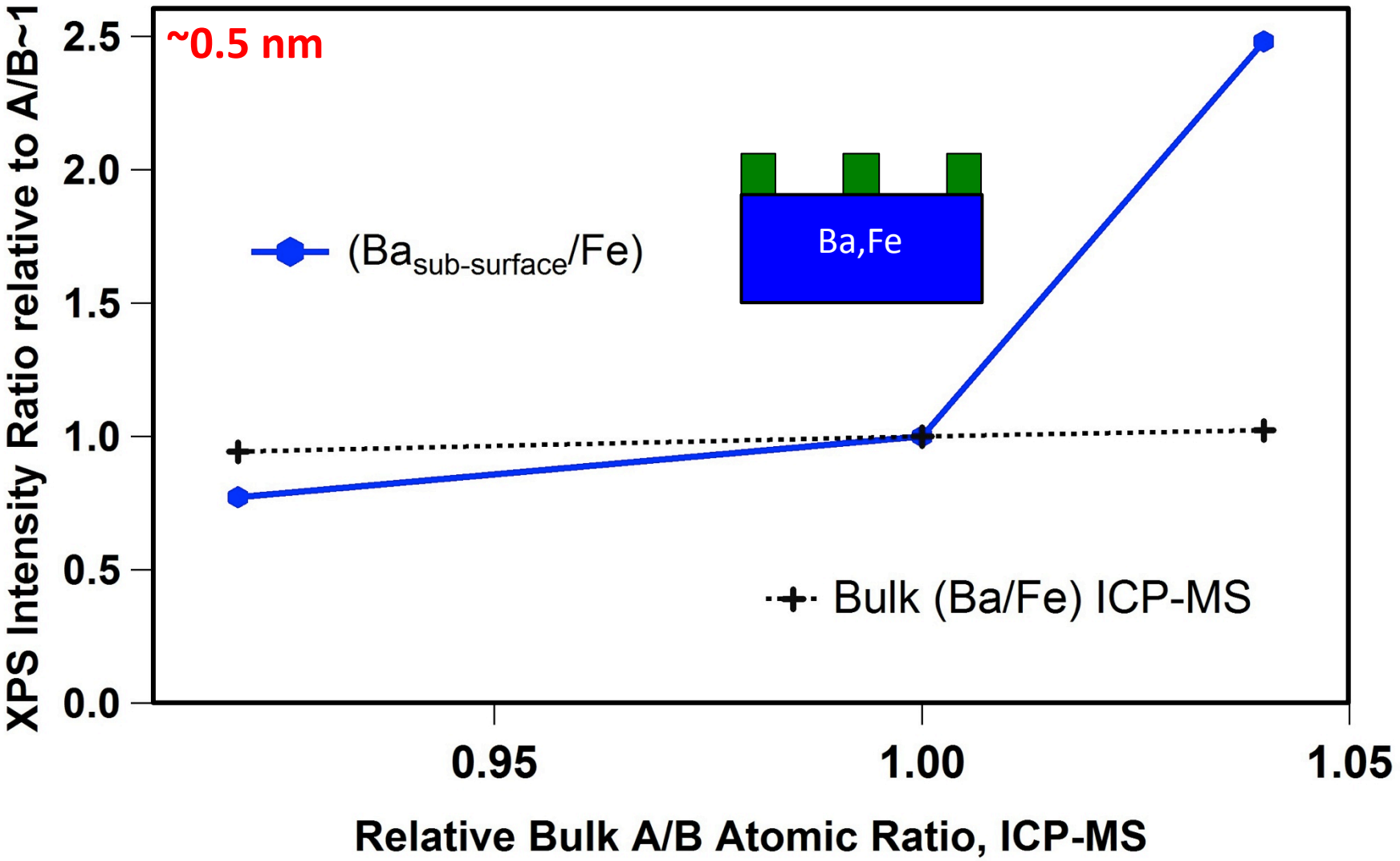


NIST 82

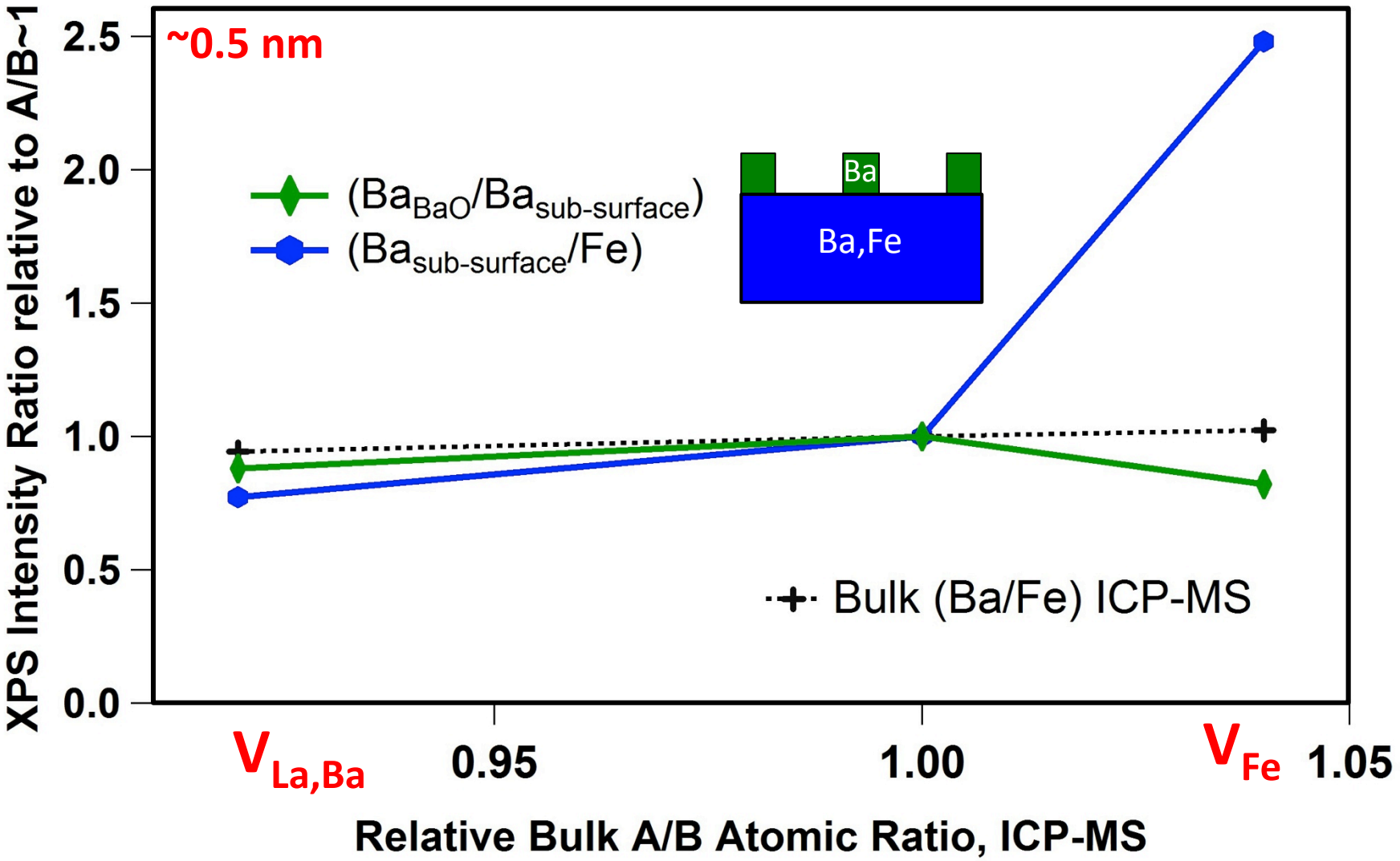
Dramatic Ba/Fe variation across samples



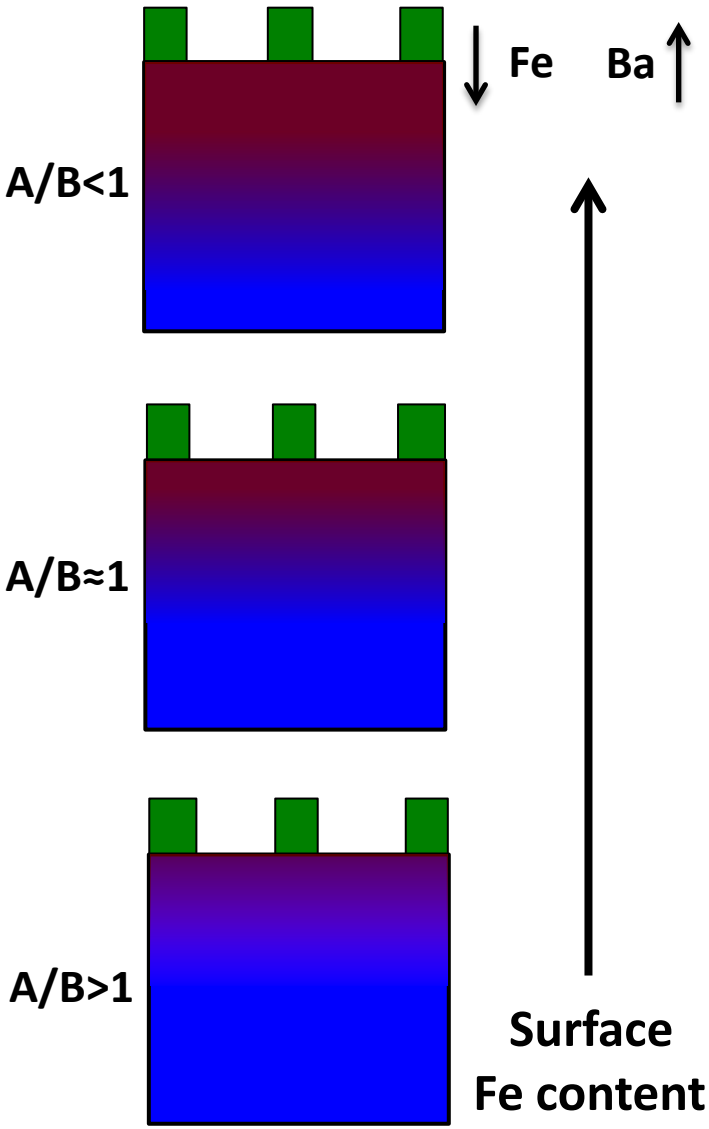
Dramatic Ba/Fe variation across samples

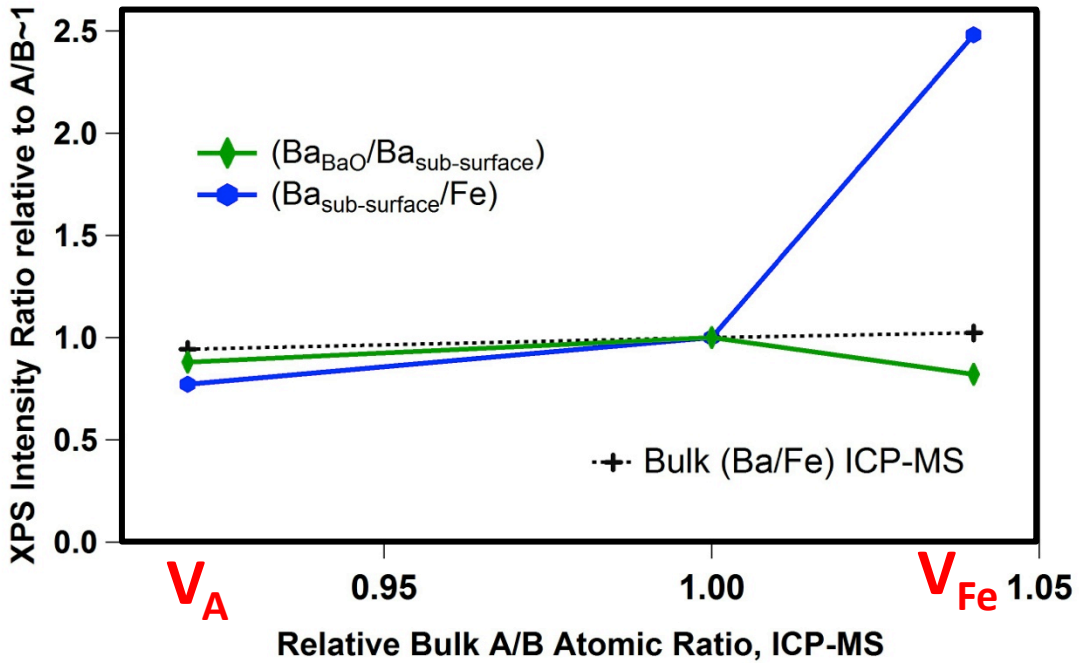


Ba surface and sub-surface ratios not changing with stoichiometry



Relative Fe surface enrichment



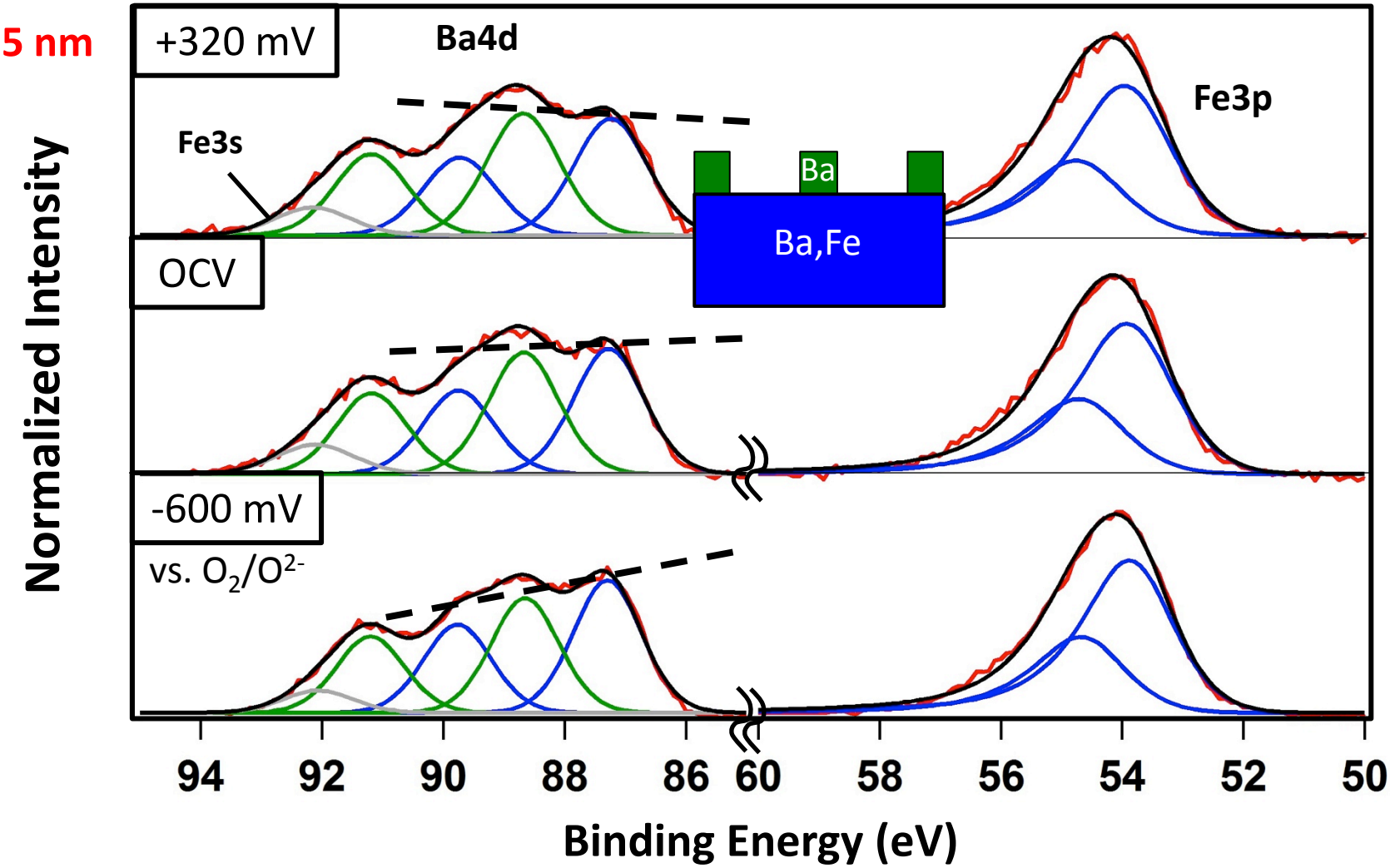


BaO

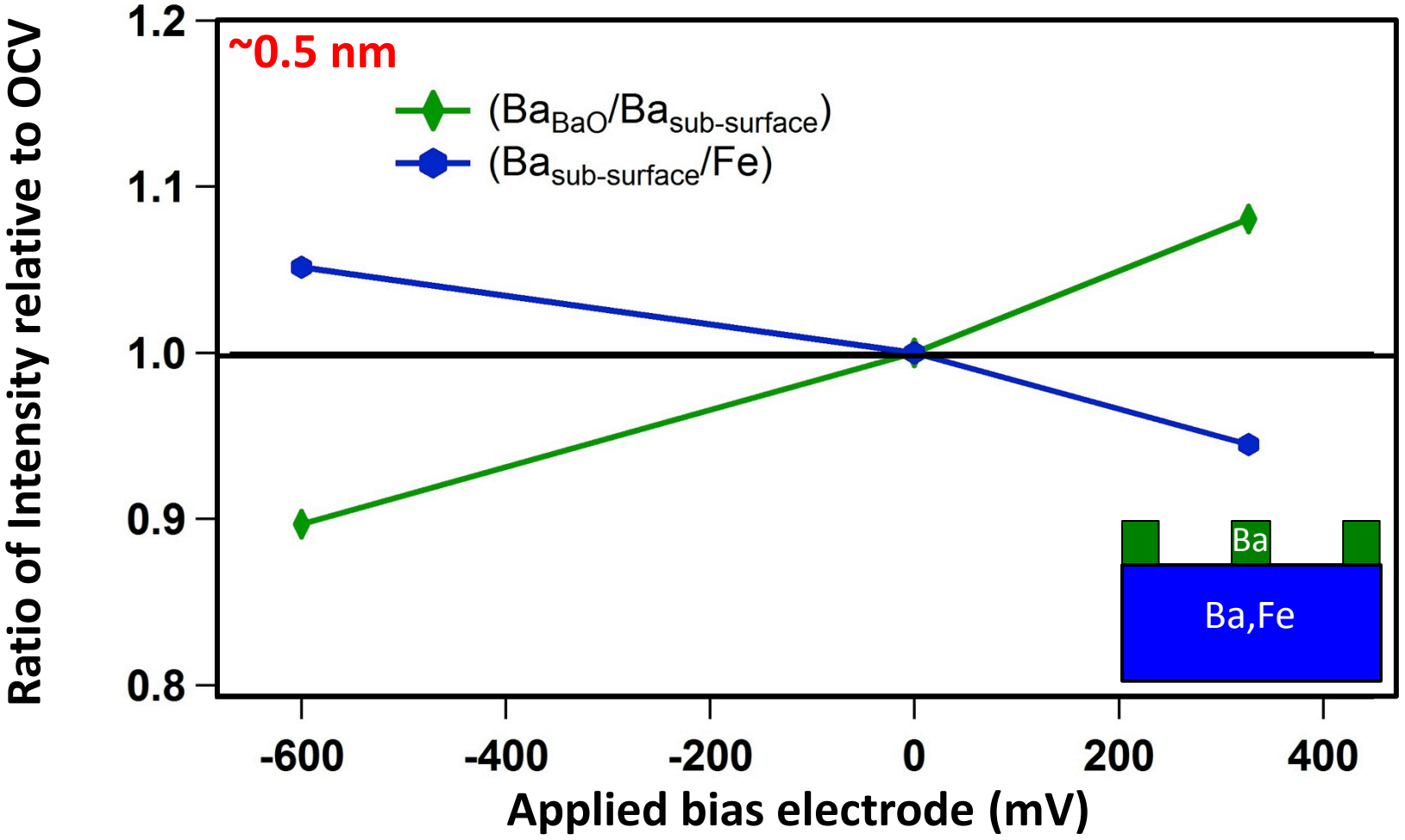
Fe enrichment

sub-Surface phase

Electrochemical Biasing : A/B<1



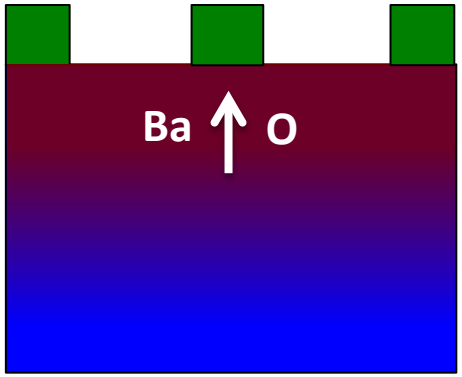
Ba in BaO and Ba in sub-Surface phase vary with electrochemical potential



e-chemical biasing affects solubility of Ba

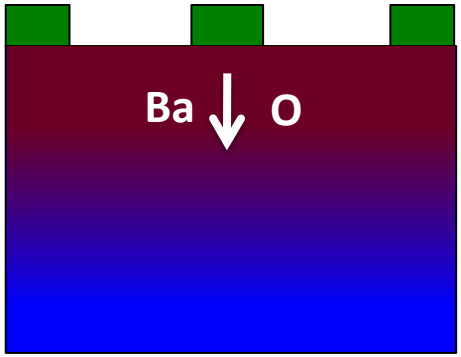
Oxygen Evolution (+)

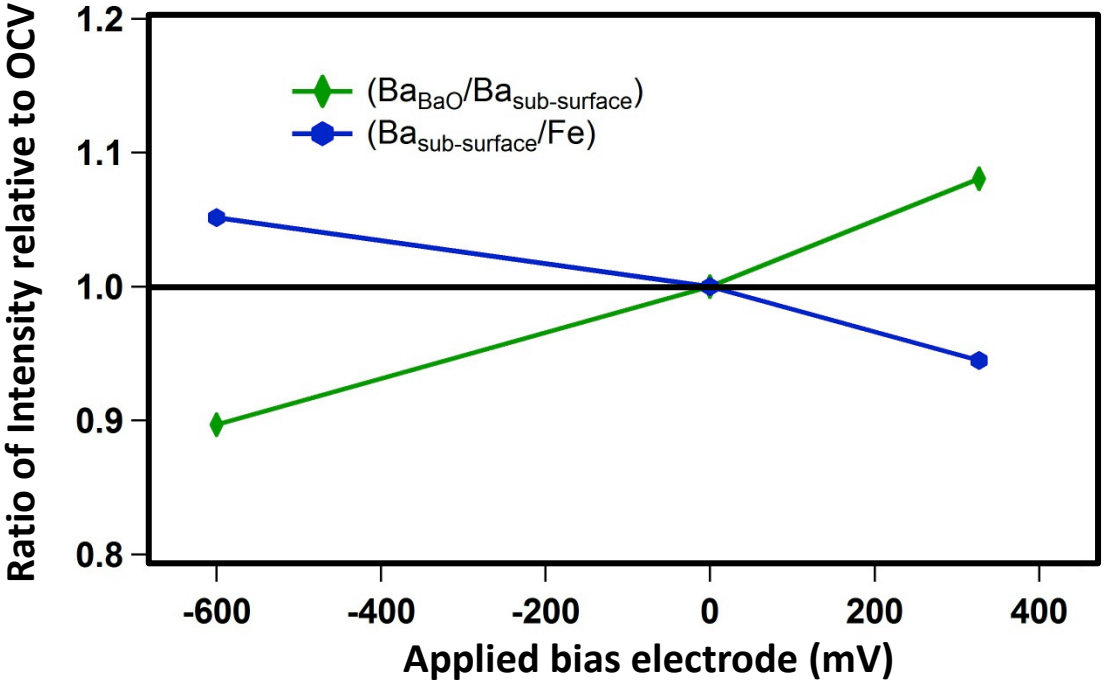
Ba less soluble



Oxygen Reduction (-)

Ba more soluble





BaO

Fe enrichment

sub-Surface phase

Future work

Expand in-situ experiments to mixed transition metal (La,AE)(Co,Fe)$O_{3-\delta}$

Fully characterize the surface composition and electronic structure under operating conditions

Develop surface modification methods based on cation-deficient and segregated active phase

Acknowledgements

Briggs White, Travis Schultz,
Joe Stoffa

Core Technology Program

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Tony McDaniel

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May Ng

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Negligible change in Fe2p with bias