Surface Chemistry, Electronic Structure, and Activity of SOFC Cathode Films

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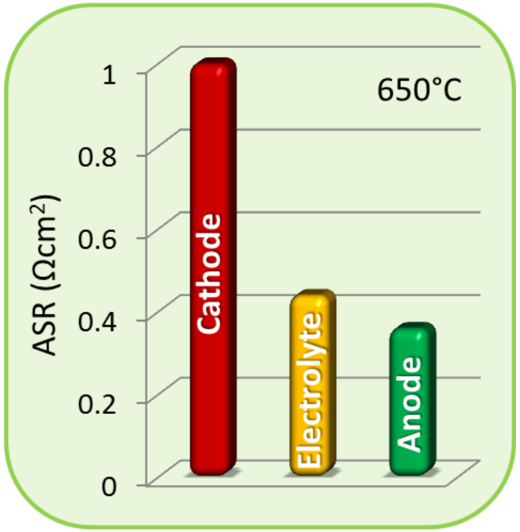
July 25, 2012

Solid Oxide Fuel Cells Cathode Materials

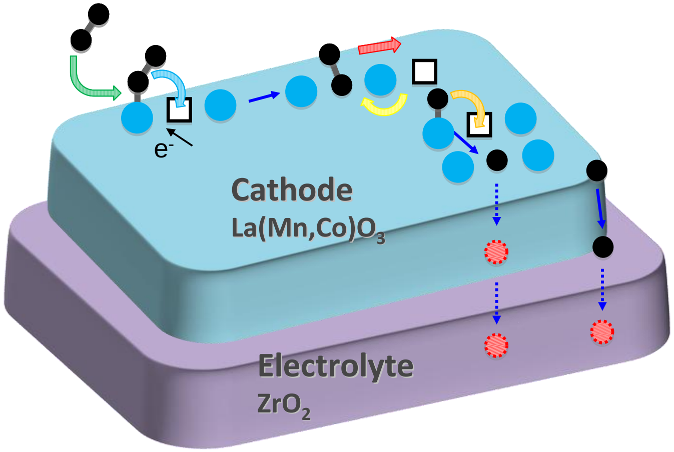
- SOFC ***cathode*** materials
  : Main barrier to achieve higher power

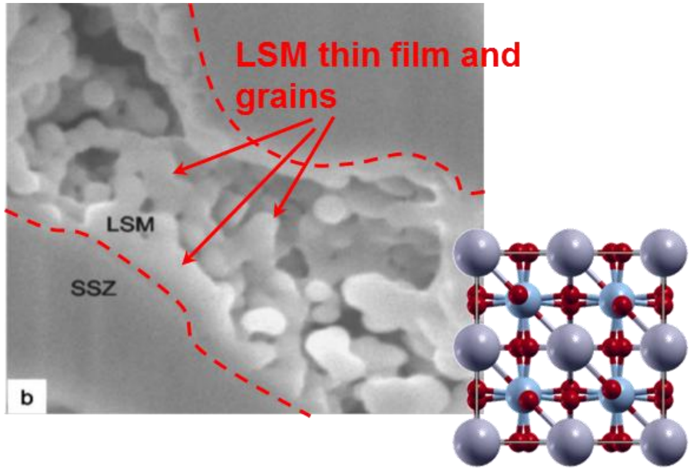


Singhal and Kendall, *High Temperature Solid Oxide Fuel Cells*, **2003**.

- Oxygen Reduction (OR) at SOFC cathode

  Structure
  Composition ←→ OR kinetic
  Electronic structure

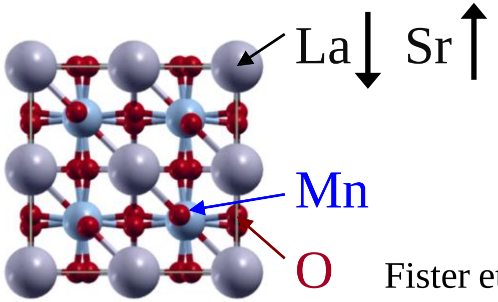




Sholklapper et al., *Electrochem. Solid. St.* **10** (2007).

Surface Structure and Chemistry: A-Site Rich?

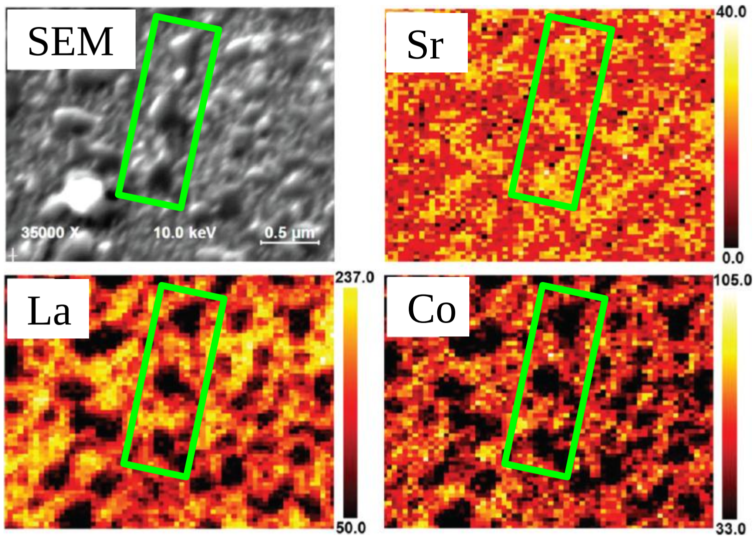
- Sr rich in A-site [1]



Fister et al., *Appl. Phys. Lett.* **93** (2008).

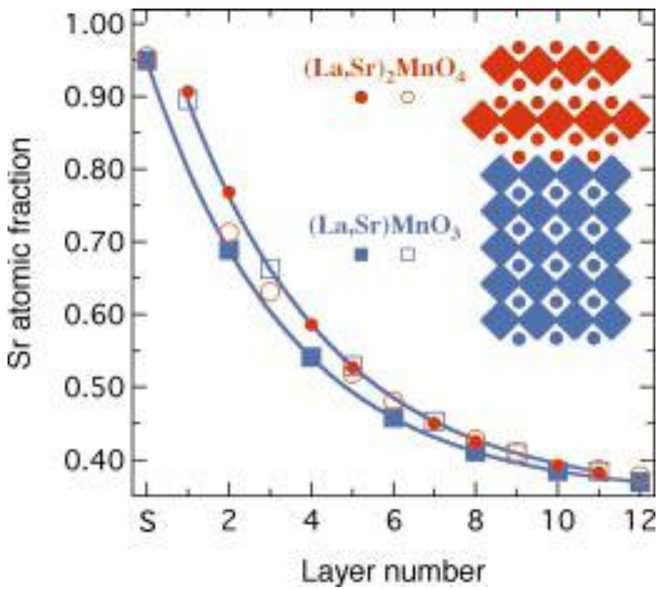
- Formation of (La,Sr)O [2]

$(La,Sr)CoO_3$ annealed at 650 C in air



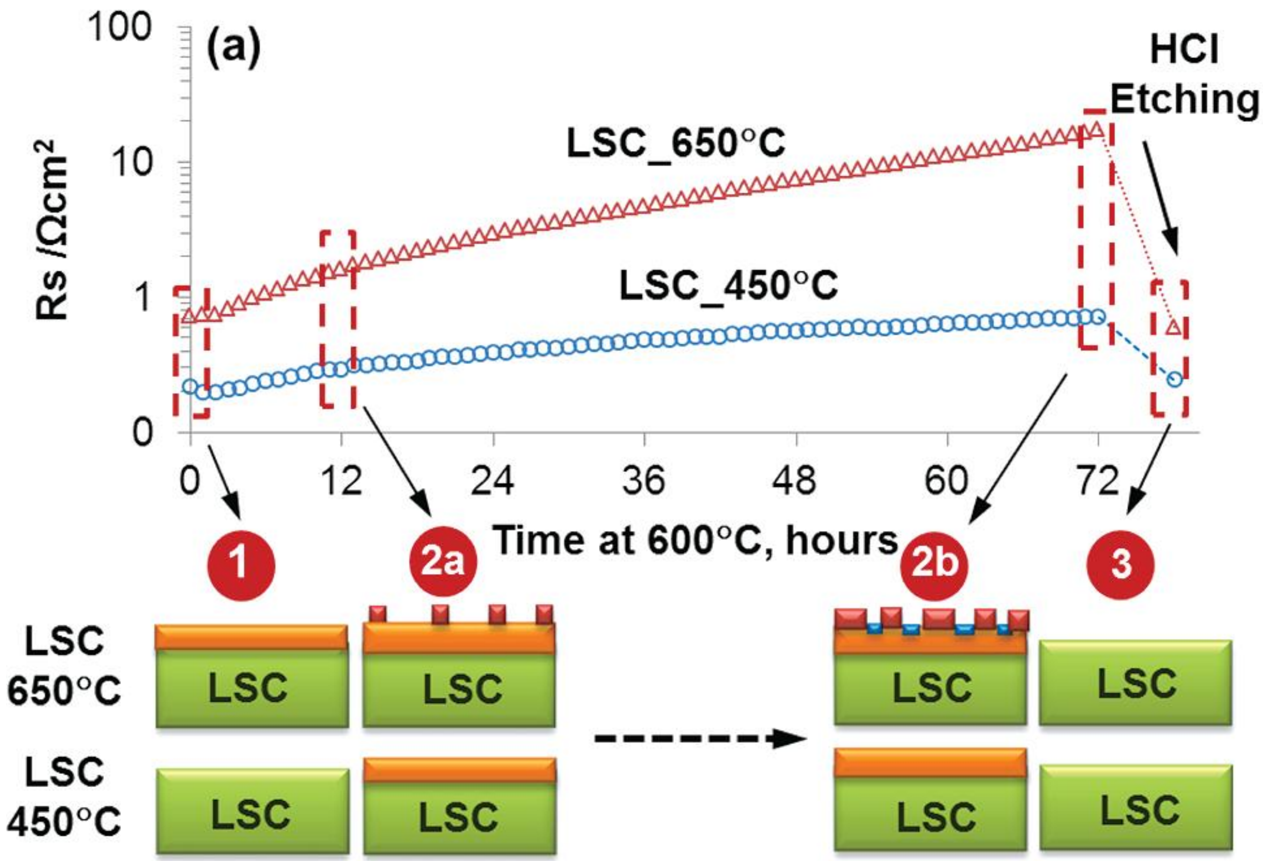
Cai et al., *Chem. Mater.* **24** (2012).

- Formation of $(La,Sr)_2MnO_4$ [3]



Dulli et al., *Phys. Rev. Lett.* **62** (2000).

Surface Chemistry Strongly Affects Surface Activity

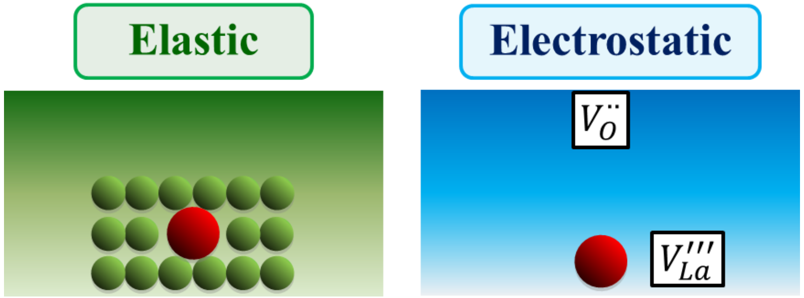


To control cation segregation for enhanced activity & stability, driving forces must be quantitatively understood

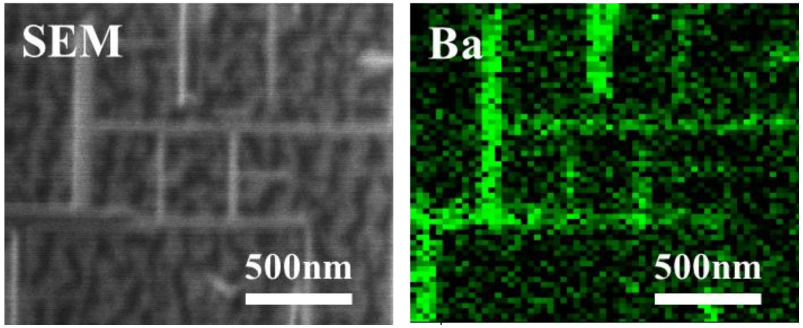
Kubicek et al., *J. Electrochem. Soc.* **158** (2011); Cai et al., *Chem. Mater.* **24** (2012)

Objective

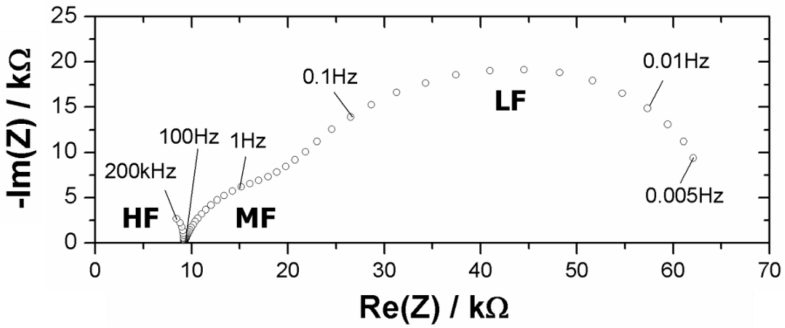
- Quantitatively assess the ***key driving forces*** of cation segregation on perovskite oxide surfaces



- Determine the ***chemical composition*** and ***structure*** of secondary phases on the surface upon cation enrichment

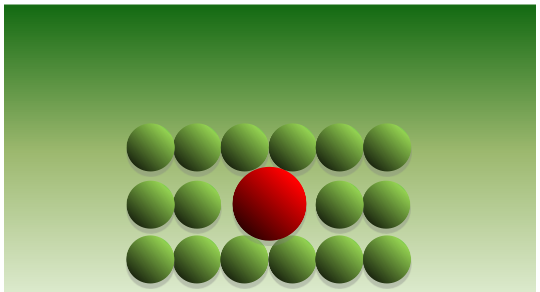


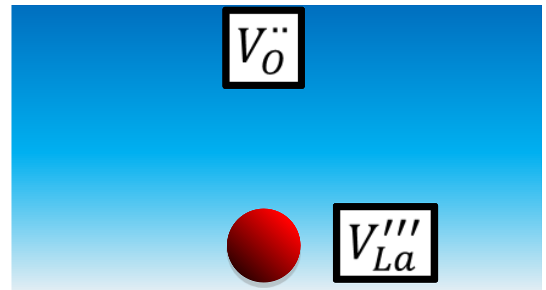
- Assess the effects on ***electrochemical*** activity



Hypothesis for Cation Segregation in Perovskites

Elastic + **Electrostatic**





Elastic energy minimization

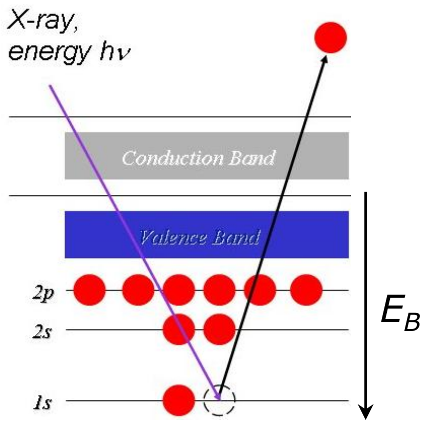
Electrostatic repulsion minimization

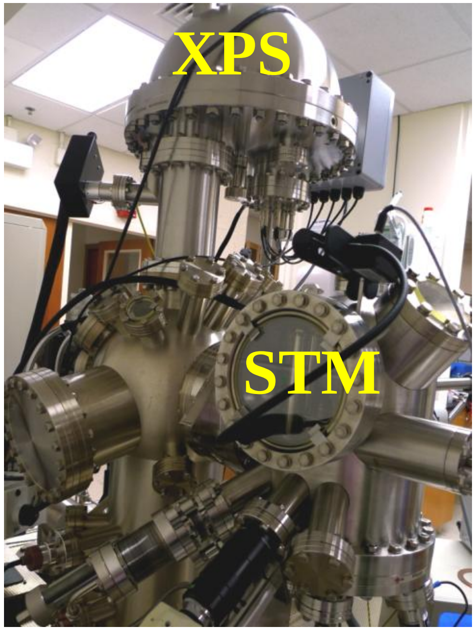
Cation Segregation

Approach

Surface Chemical State

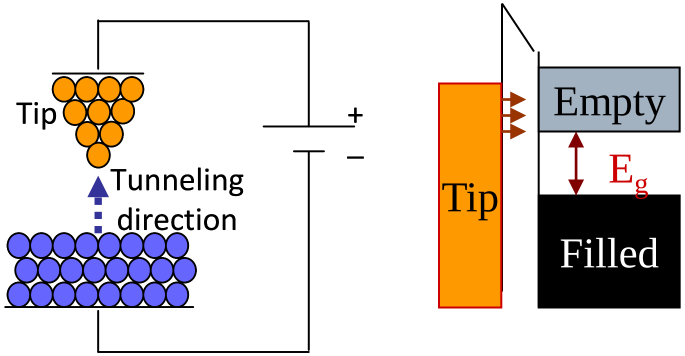
X-ray Photoelectron Spectroscopy (XPS)
Nanoscale Auger Electron Spectroscopy (n-AES)





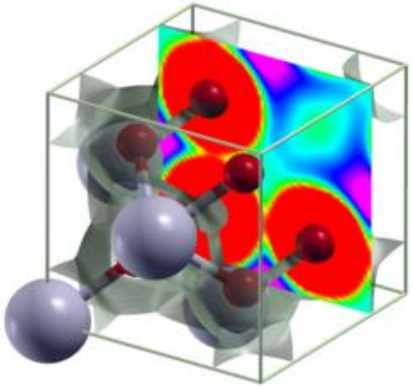
Surface Electronic Structure

Scanning Tunneling Microscopy / Spectroscopy (STM/STS), ***in situ***

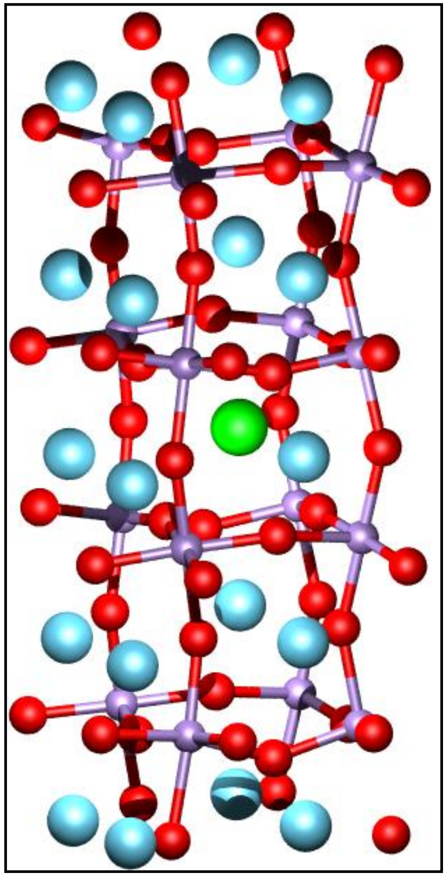


Mechanisms, Energetics and Kinetics of Cation Segregation

Electronic structure (DFT+U)



Control of Elastic Interactions



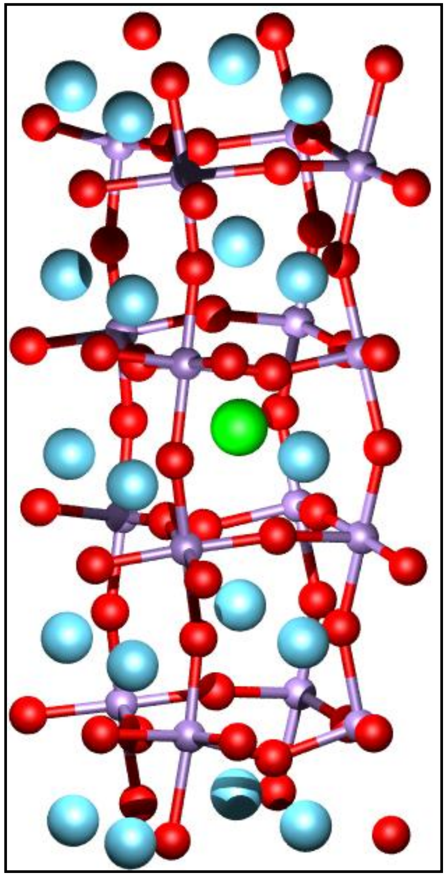
$LaMnO_3$ or $SmMnO_3$

To systematically induce ***elastic energy differences***, radius of the selected dopant cations is varied.

Host		Dopant		
		Ca^{2+}	Sr^{2+}	Ba^{2+}
La^{3+}	Δr (Å)	-0.02	0.08	0.25
	$\Delta r/r_0$ (%)	-1.5	5.9	18.4
Sm^{3+}	Δr (Å)	0.10	0.20	0.37
	$\Delta r/r_0$ (%)	8.1	16.1	29.8

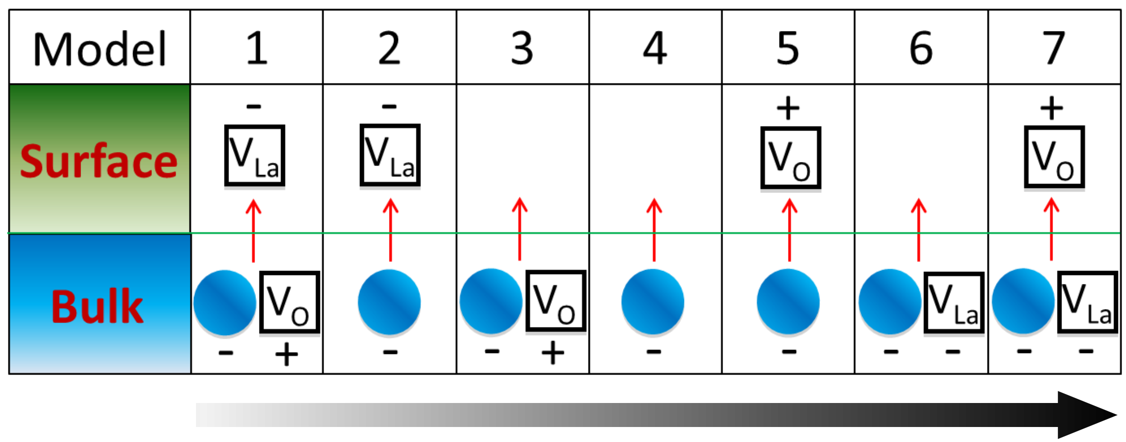
Increasing ***dopant size*** relative to the host cation

Control of Electrostatic Interactions



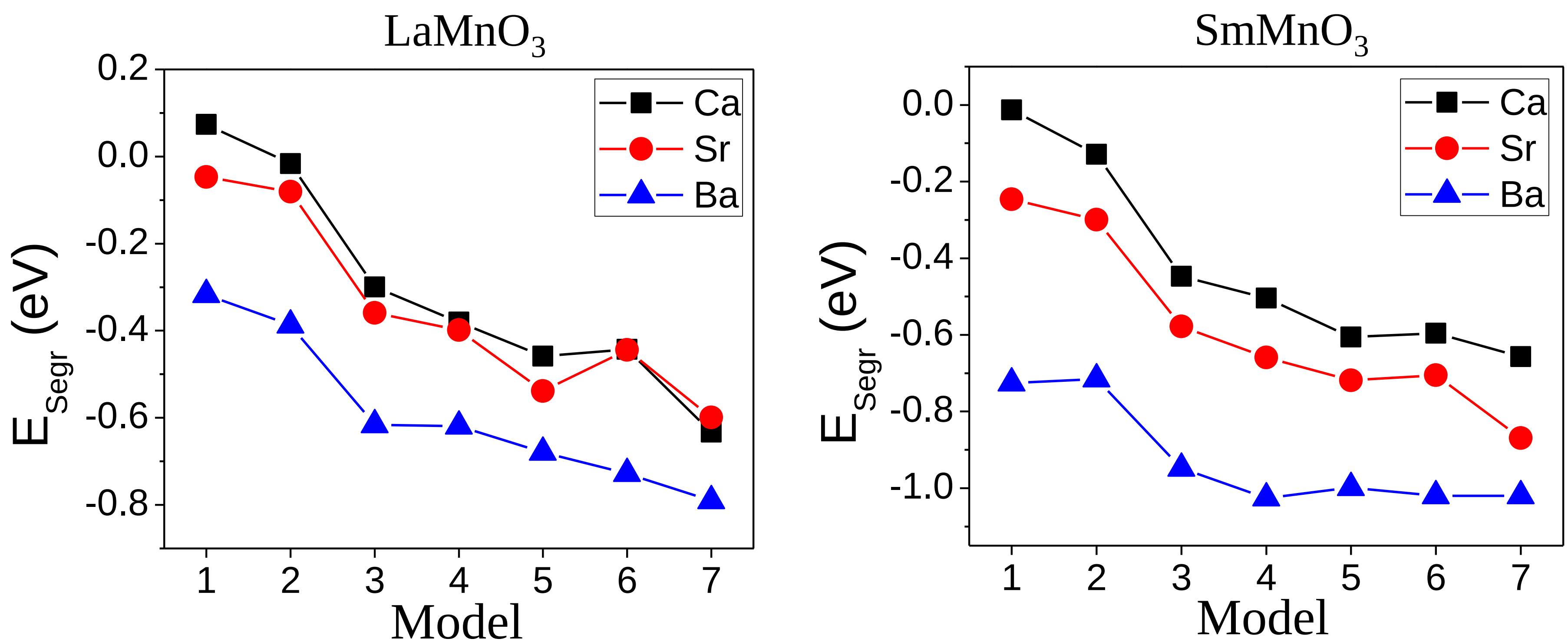
$LaMnO_3$ or $SmMnO_3$

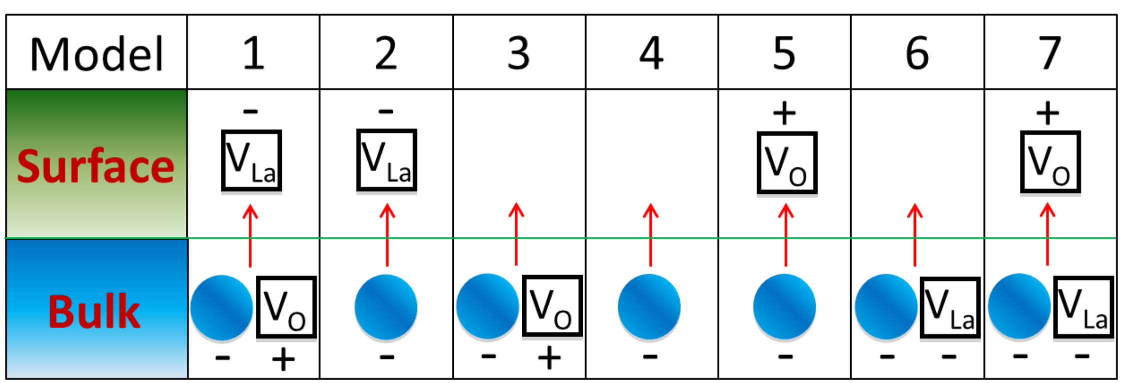
Seven models to represent the variation of ***electrostatic interactions*** are constructed by controlling the distribution of charged oxygen- and cation-vacancies.



Increasing ***attractive interaction*** to the dopant cation to the surface

Both Elastic and Electrostatic Drivers are Important



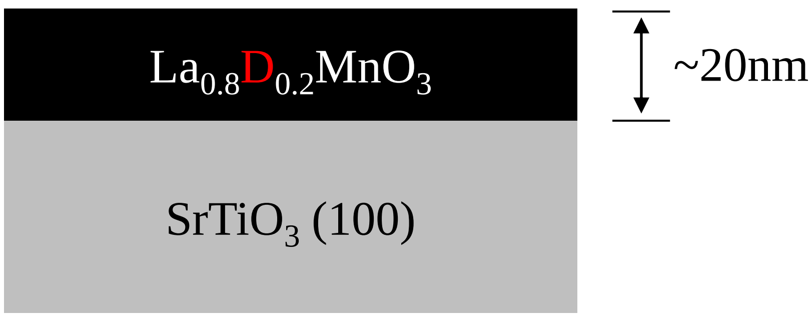


Han and Yildiz,
in preparation.

Elastic Interaction: Dopant Size Mismatch

To systematically induce elastic energy differences, radius of the selected dopant cations is varied.

Host cation	Size mismatch	Dopant		
		Ca^{2+}	Sr^{2+}	Ba^{2+}
La^{3+}	Δr (= $r_{host} - r_{dopant}$) (Å)	-0.02	0.08	+0. 25
	$\Delta r/r_0$ (%)	-1.5	+5.9	+18.4



$La_{0.8}Ba_{0.2}MnO_3$ **LBM**

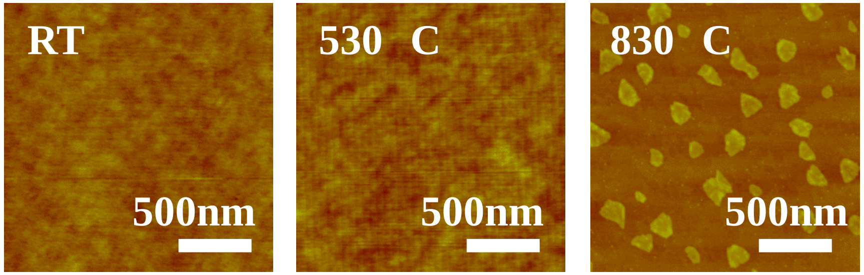
$La_{0.8}Sr_{0.2}MnO_3$ **LSM**

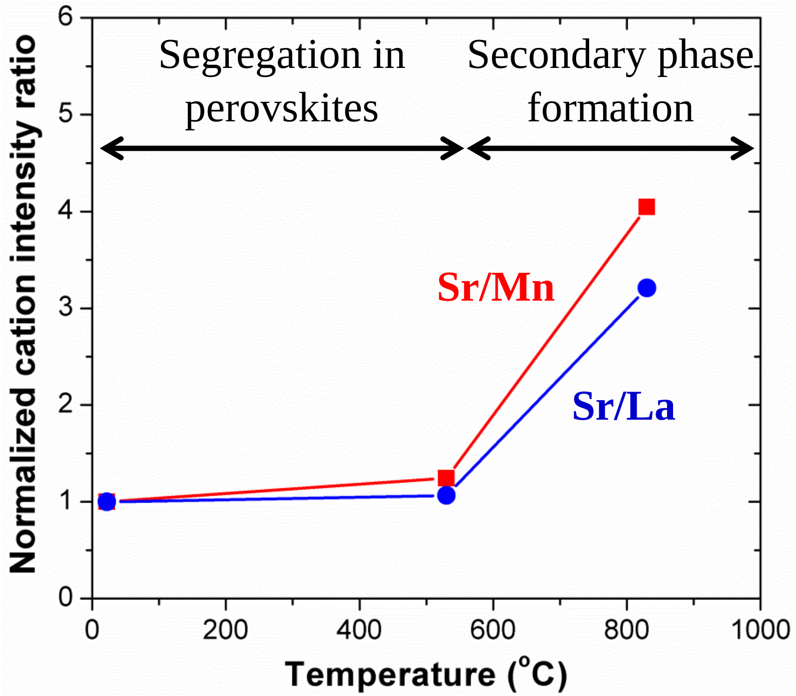
$La_{0.8}Ca_{0.2}MnO_3$ **LCM**

Pulse laser deposition (T = 815 °C in pO_2 = 10 mTorr)

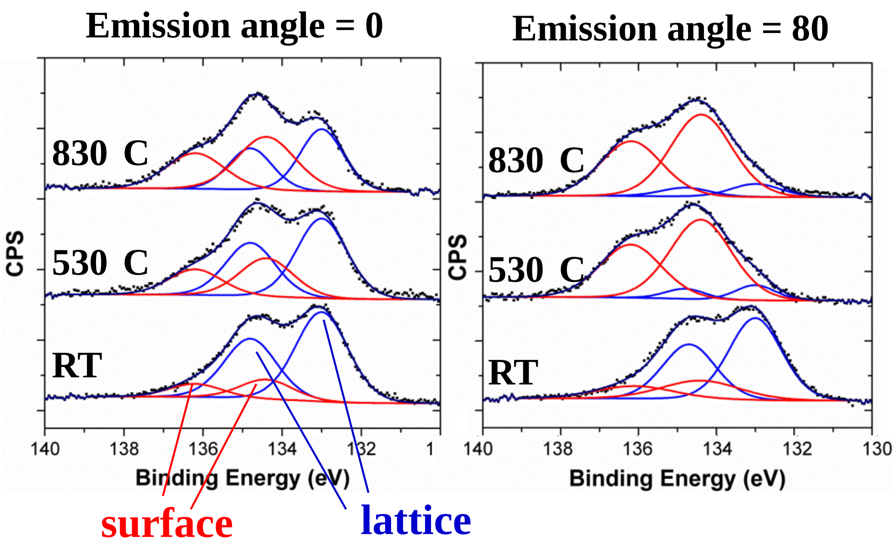
Annealing Induced Changes

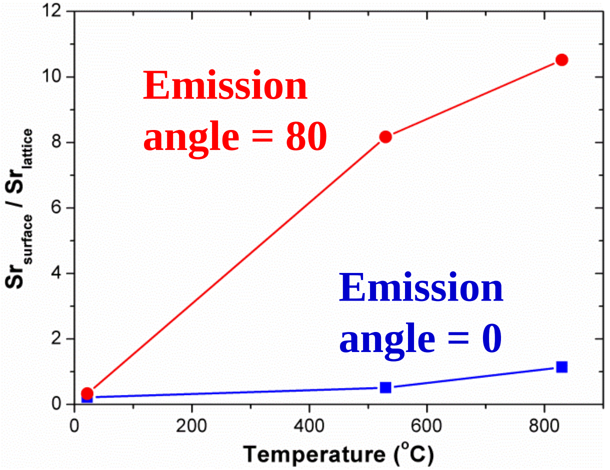
Structural changes (AFM)



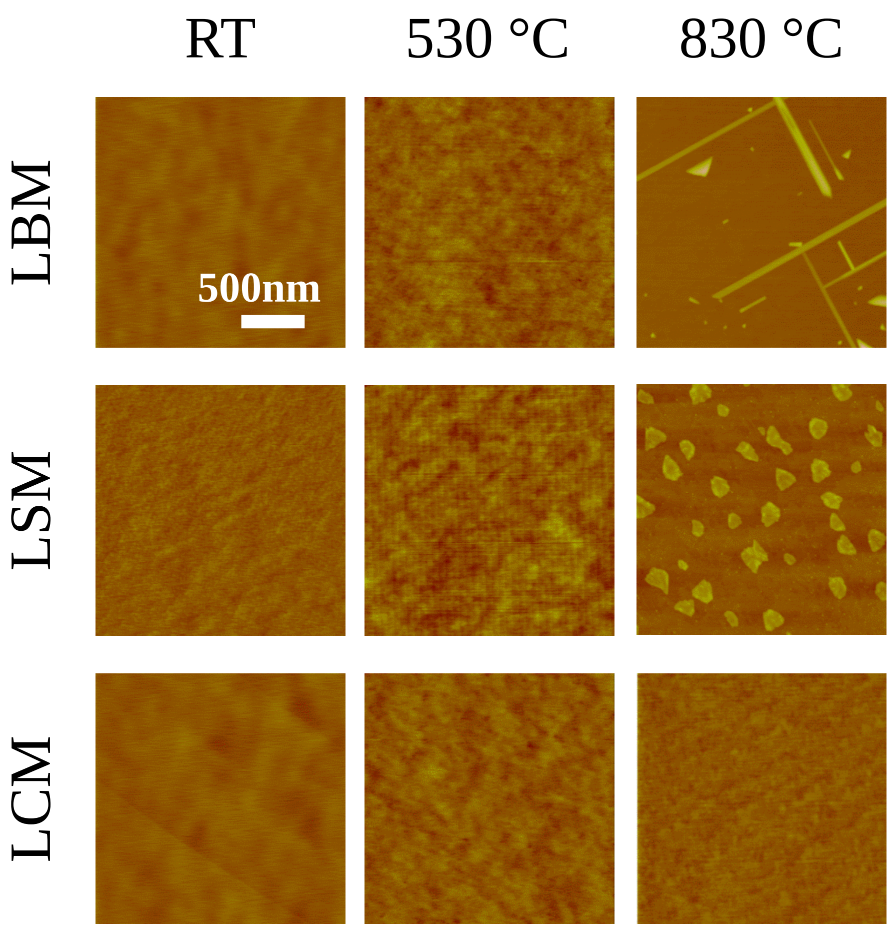


Chemical changes (Sr 3d)

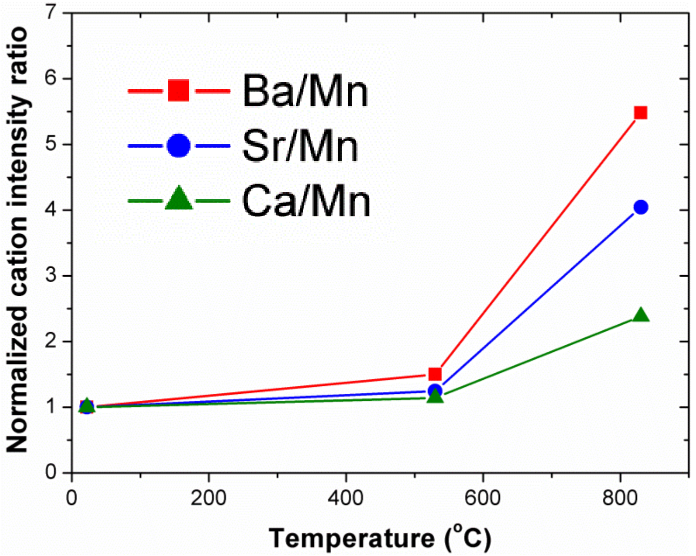


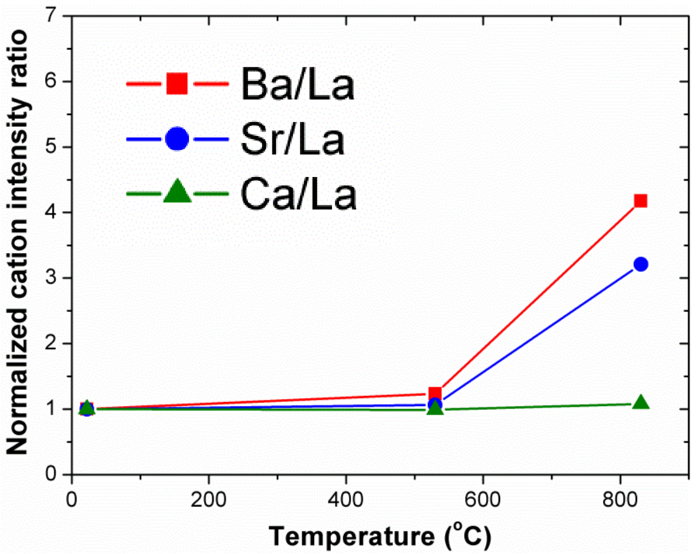


Effects of Size Mismatch on Dopant Segregation



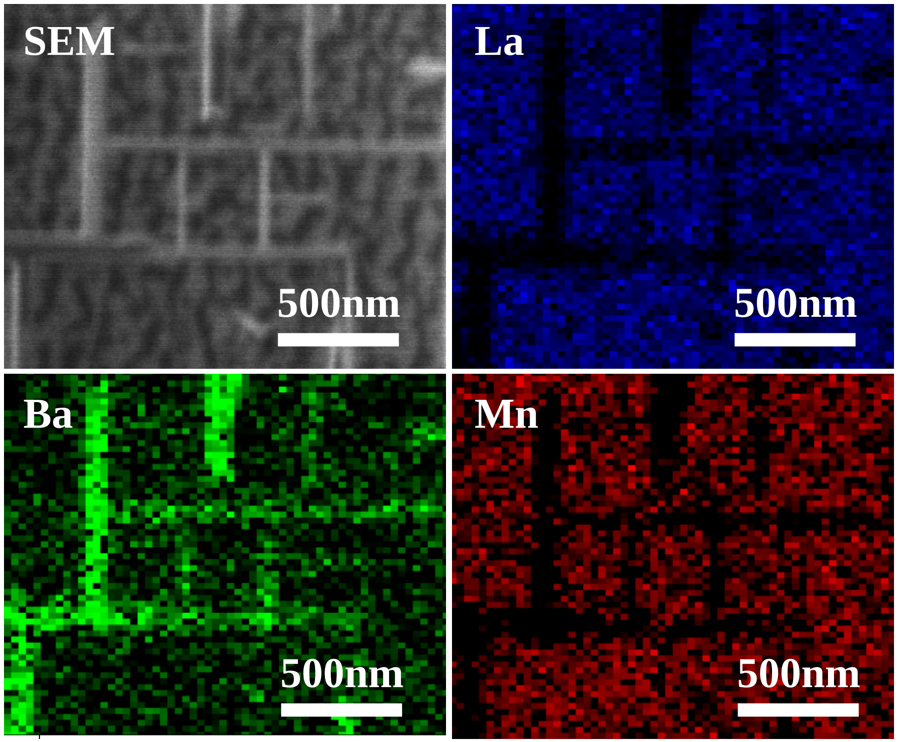
Annealing in air for 1 hr

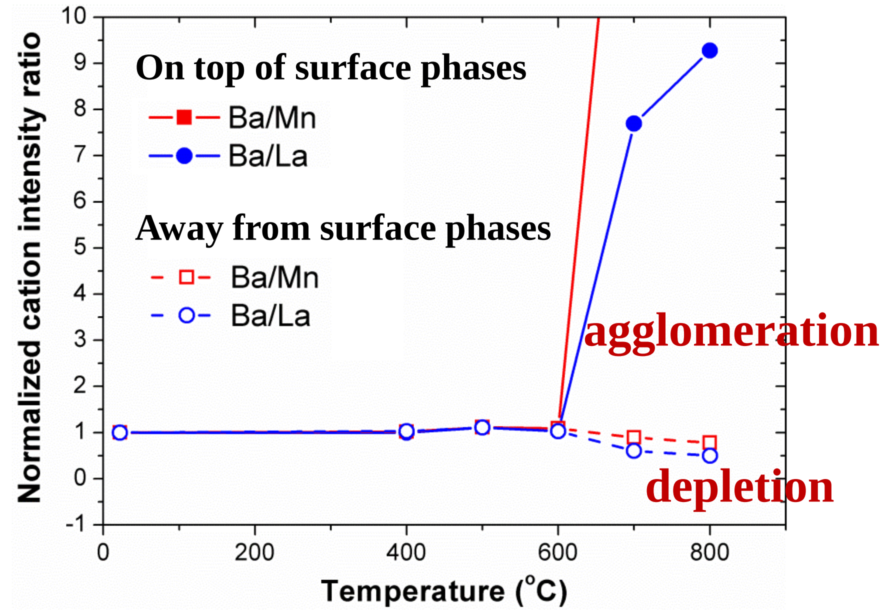




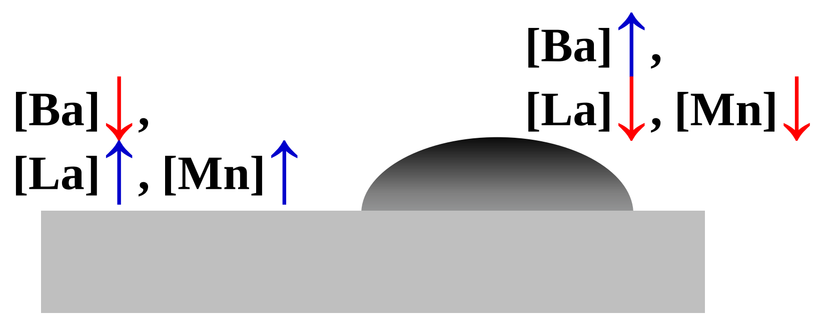
Localized Chemical Identification

LBM after annealing at 830 C

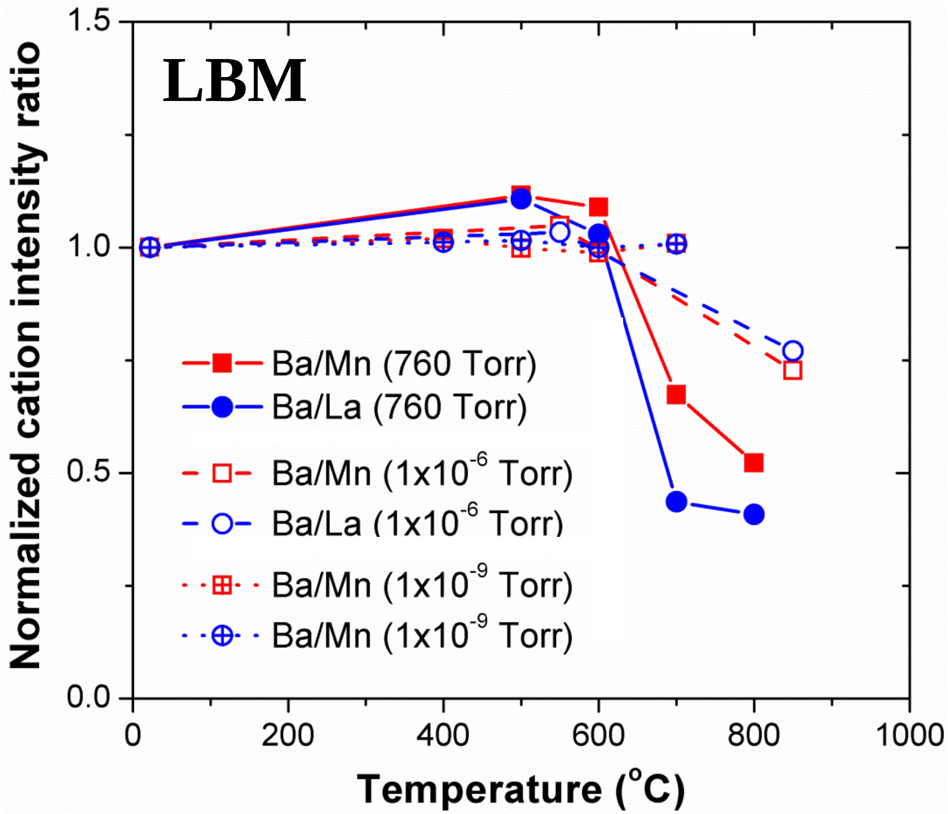


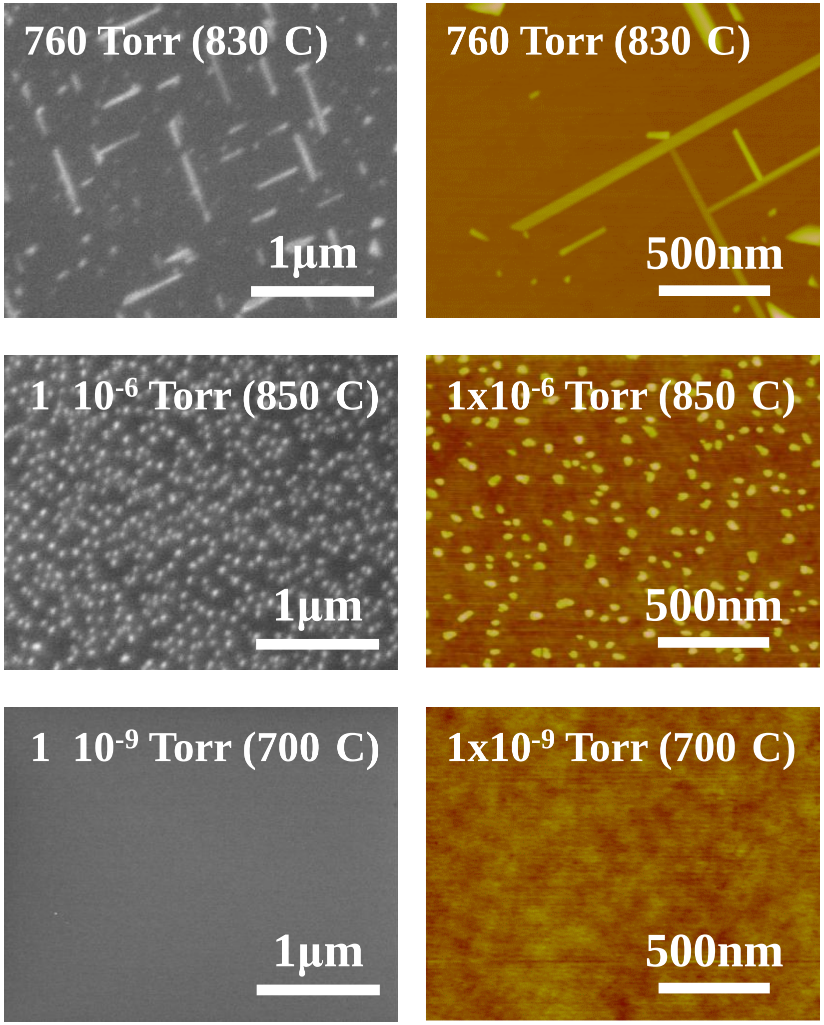


Auger electron spectroscopy: elemental mapping (left) and point spectra (right)



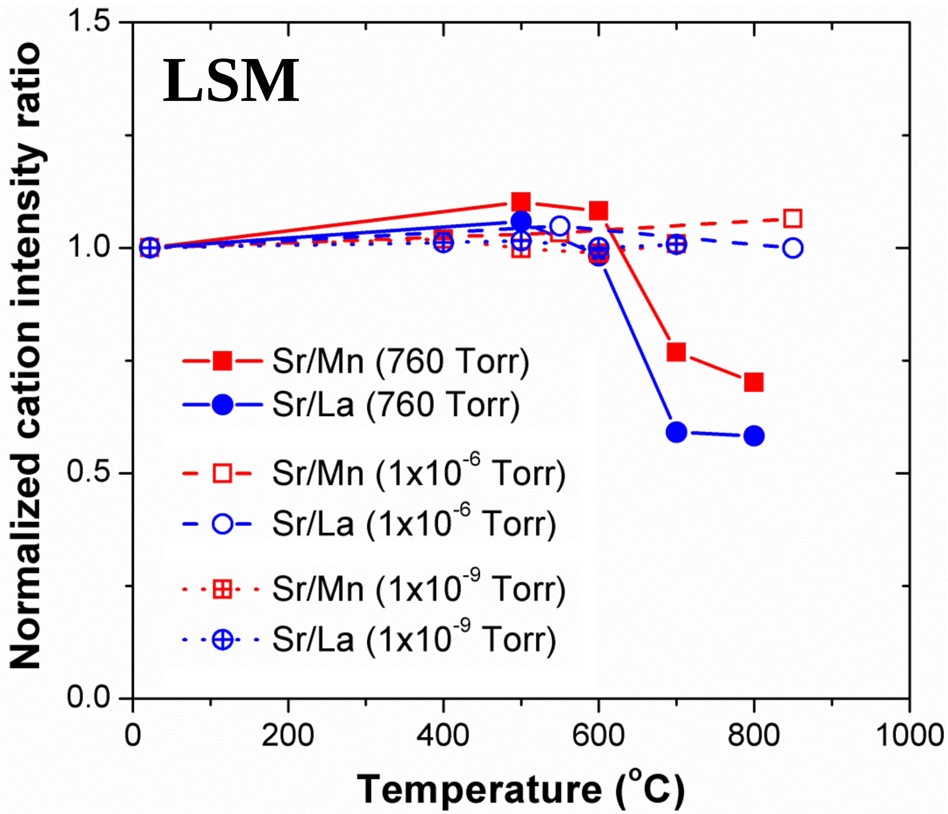
Effects of Oxygen Pressure on Dopant Segregation



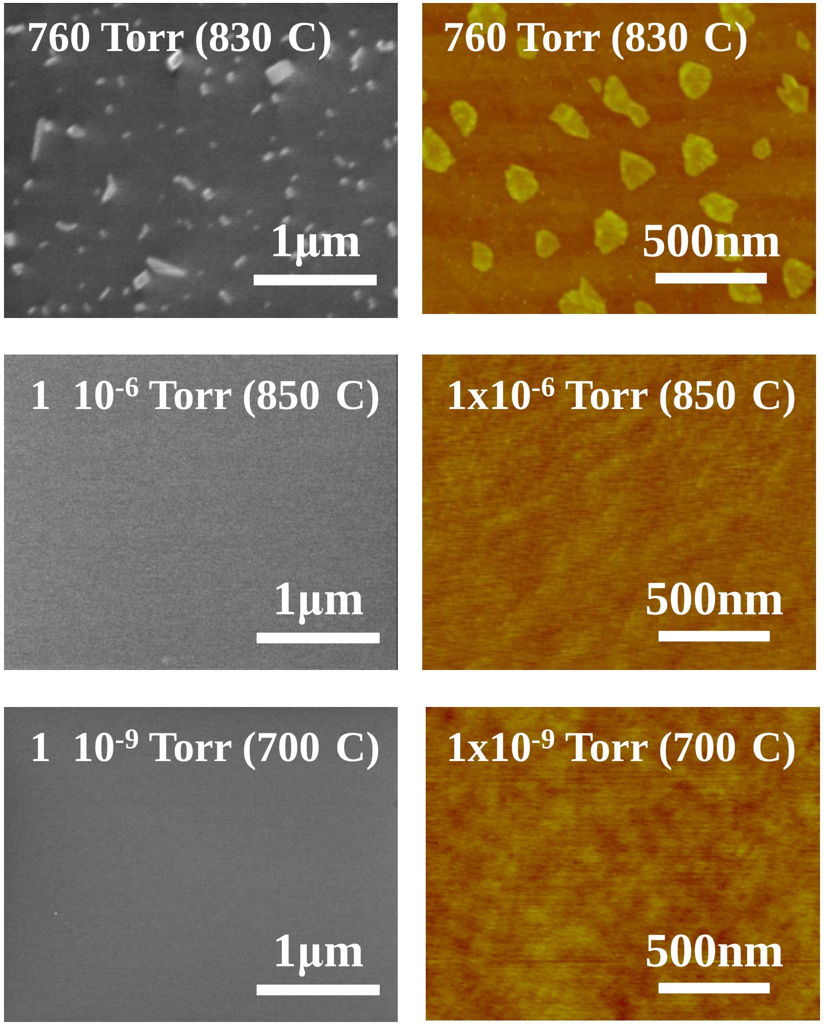


Cation intensity ratio away from the surface phases (background data was used if no features exist)

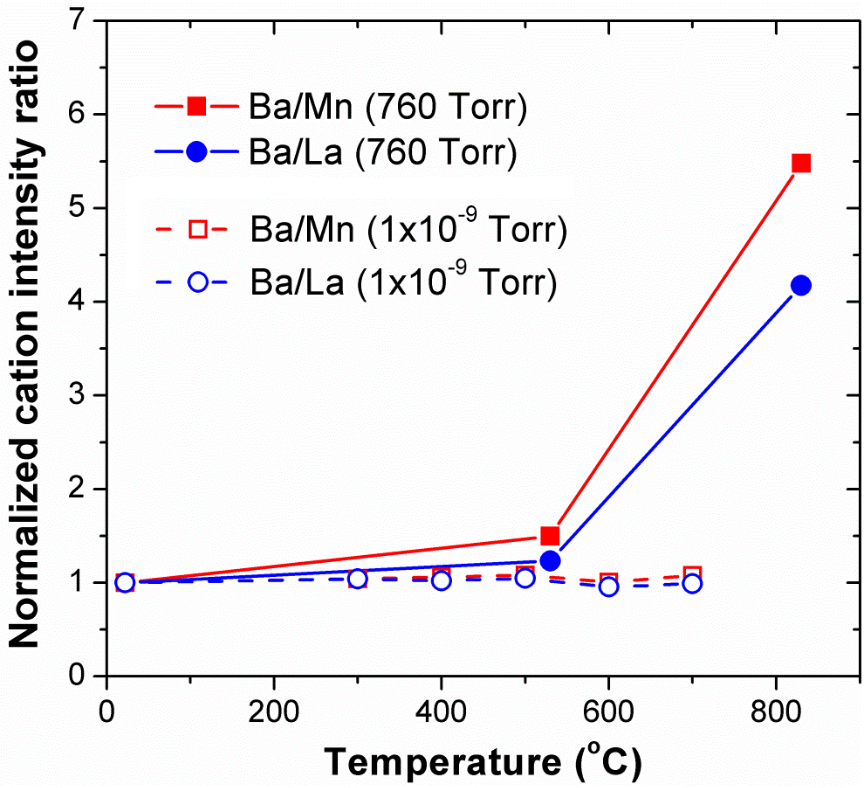
Effects of Oxygen Pressure on Dopant Segregation



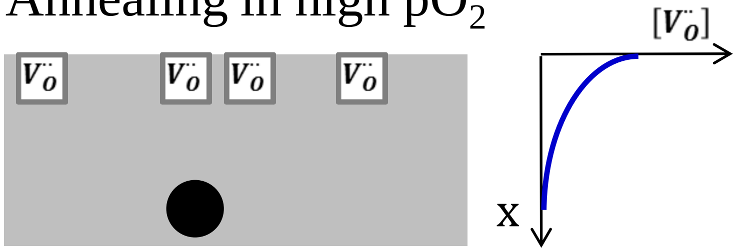
Cation intensity ratio away from the surface phases (background if no features exist)



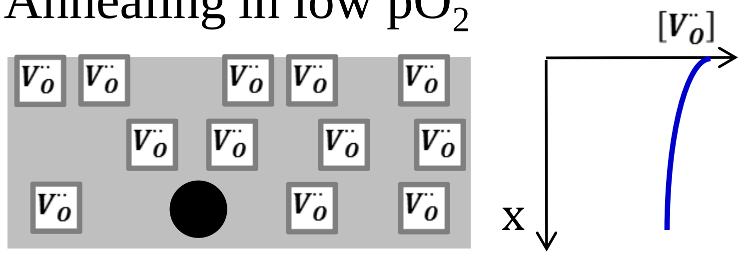
Effects of Oxygen Pressure on Dopant Segregation



Annealing in high pO_2

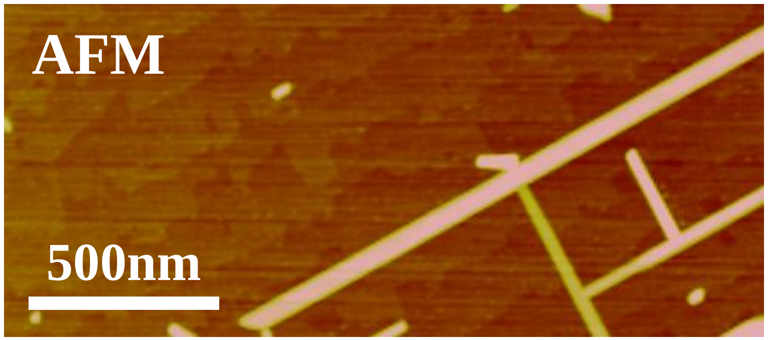


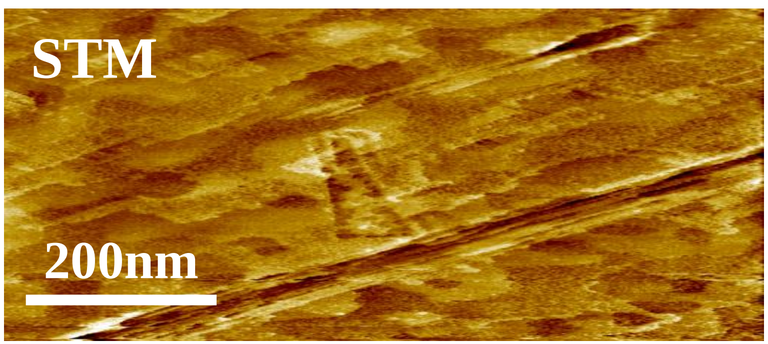
Annealing in low pO_2



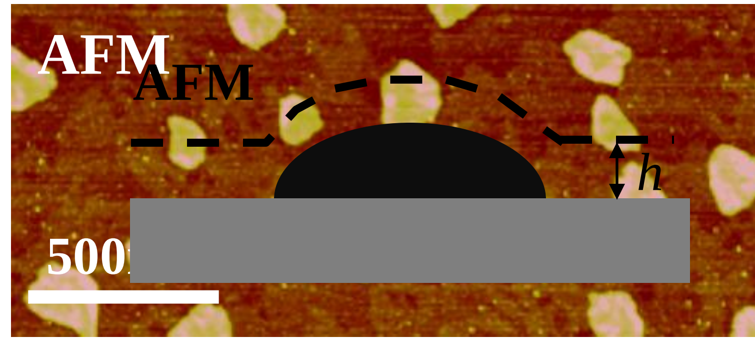
Electronic Properties of Surface Phases

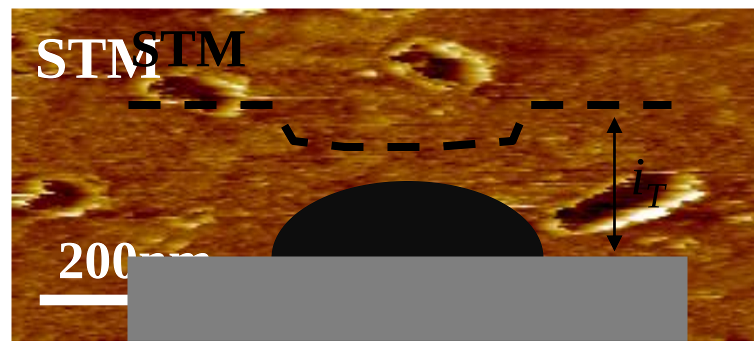
LBM annealed at 830 C in air





LSM annealed at 830 C in air



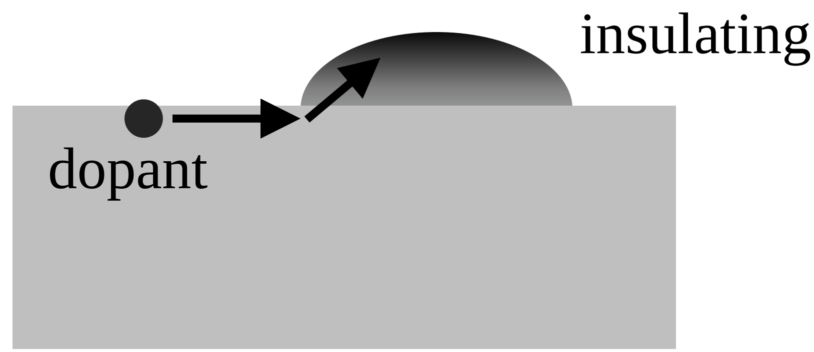


Annealing-induced surface phases are ***insulating***

($E_{g,LBM}$, $E_{g,LSM}$ ~ 2 eV, $E_{g,BaO}$ ~4.5 eV, $E_{g,SrO}$ ~ 5.7 eV)

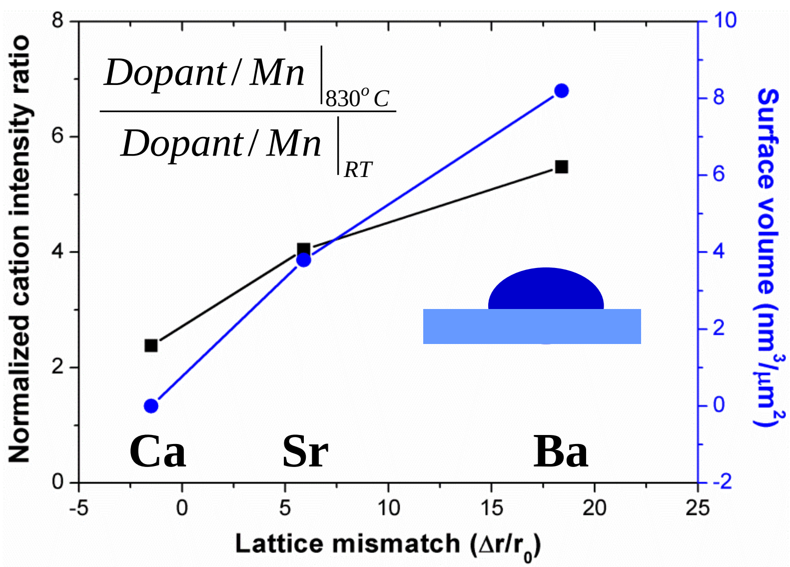
Summary

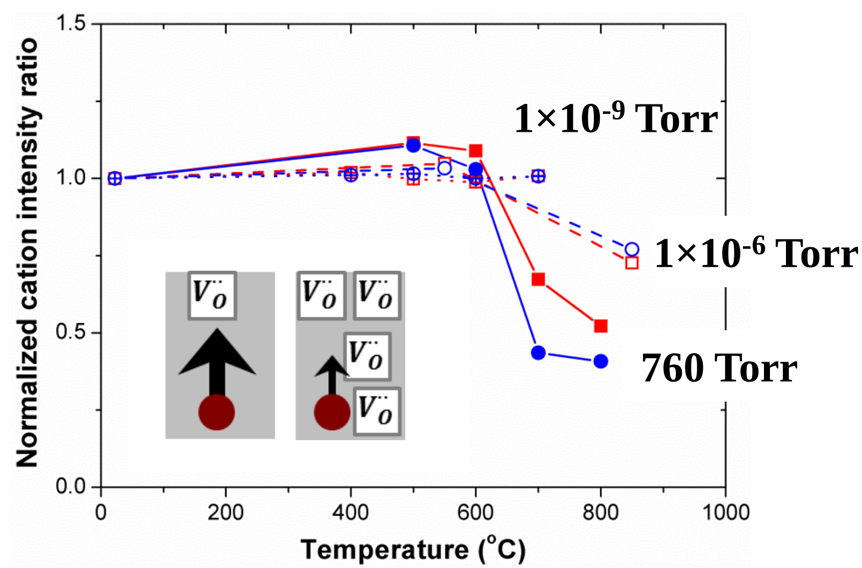
Surface segregation



Agglomeration

Segregation = Elastic + Electrostatic





Future Work

- ✓ Surface ***electronic*** structures using scanning tunneling microscopy / spectroscopy.
- ✓ ***Electrochemical*** properties using impedance spectroscopy.

Acknowledgements

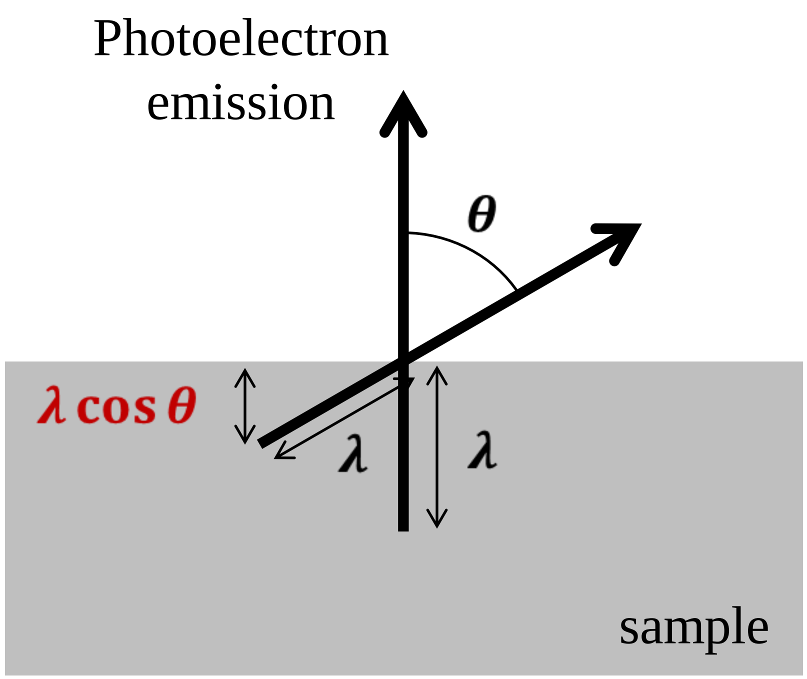
- ✓ US-DOE, Office of Fossil Energy for financial support. (Grant No. DE-NT0004117)
- ✓ Prof. C. Ross and Prof. H. L. Tuller at MIT for the use of their PLD system.

Supplementary

Angle-Resolved X-ray Photoelectron Spectroscopy

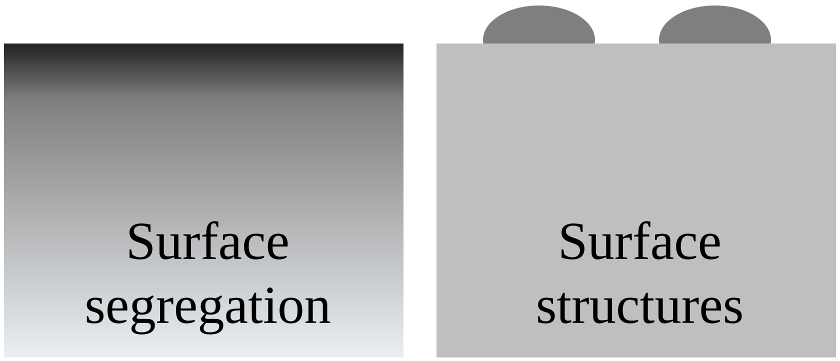
Information depth varies with an emission angle

$$I = I_{\infty} exp(-d/\lambda \cos\theta)$$

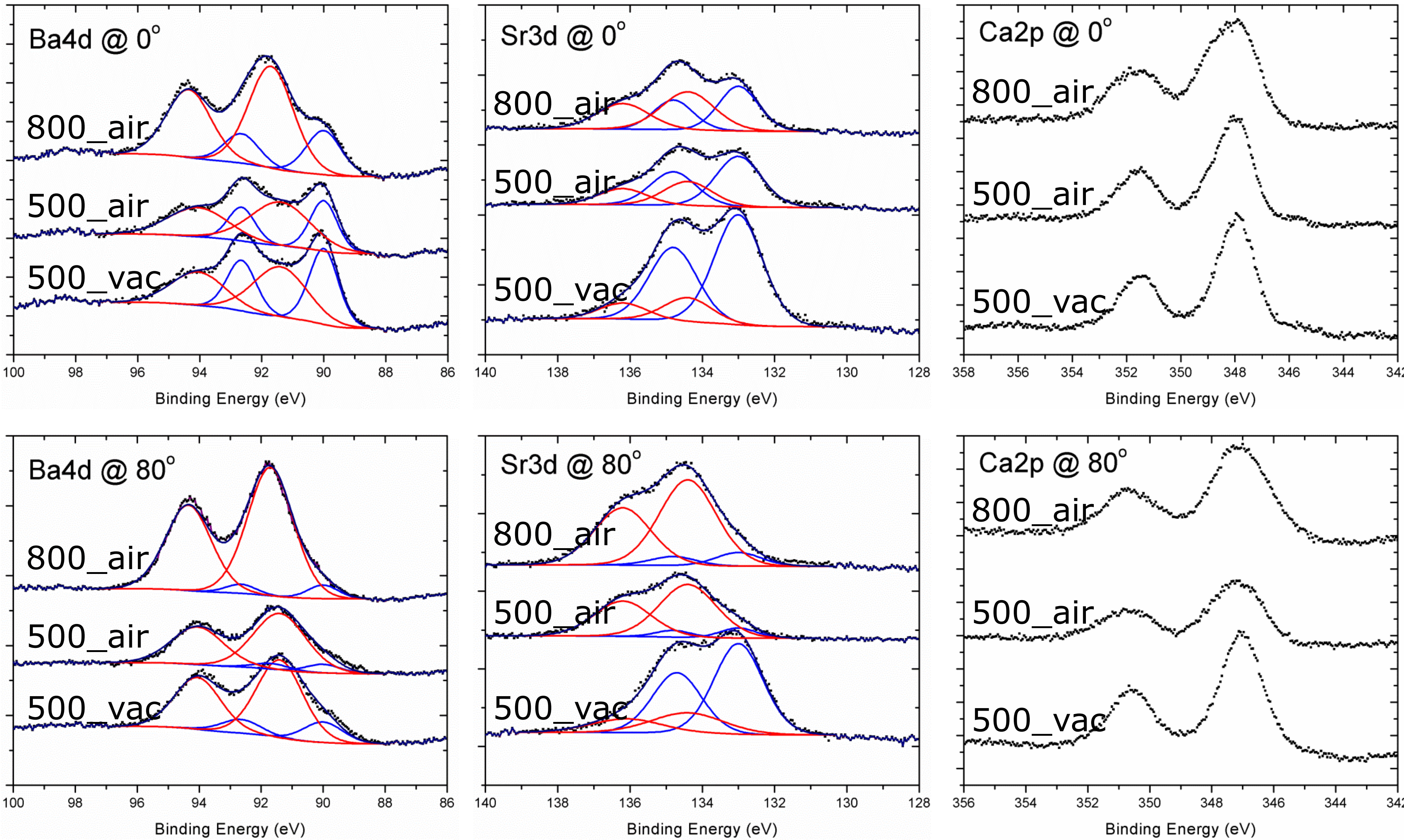


Probe the chemical composition with a depth information

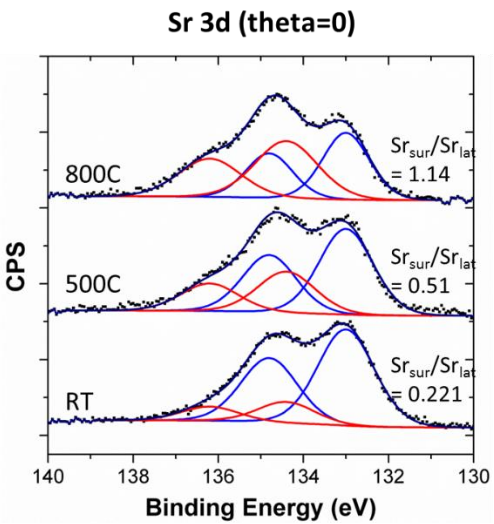
(Escape depth of Sr 3d is ~6nm with θ=0 , and ~1nm with θ=80°)

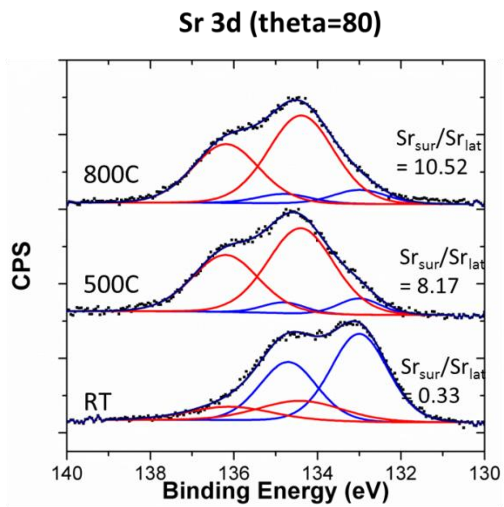


HR XPS for dopant peaks



HR XPS



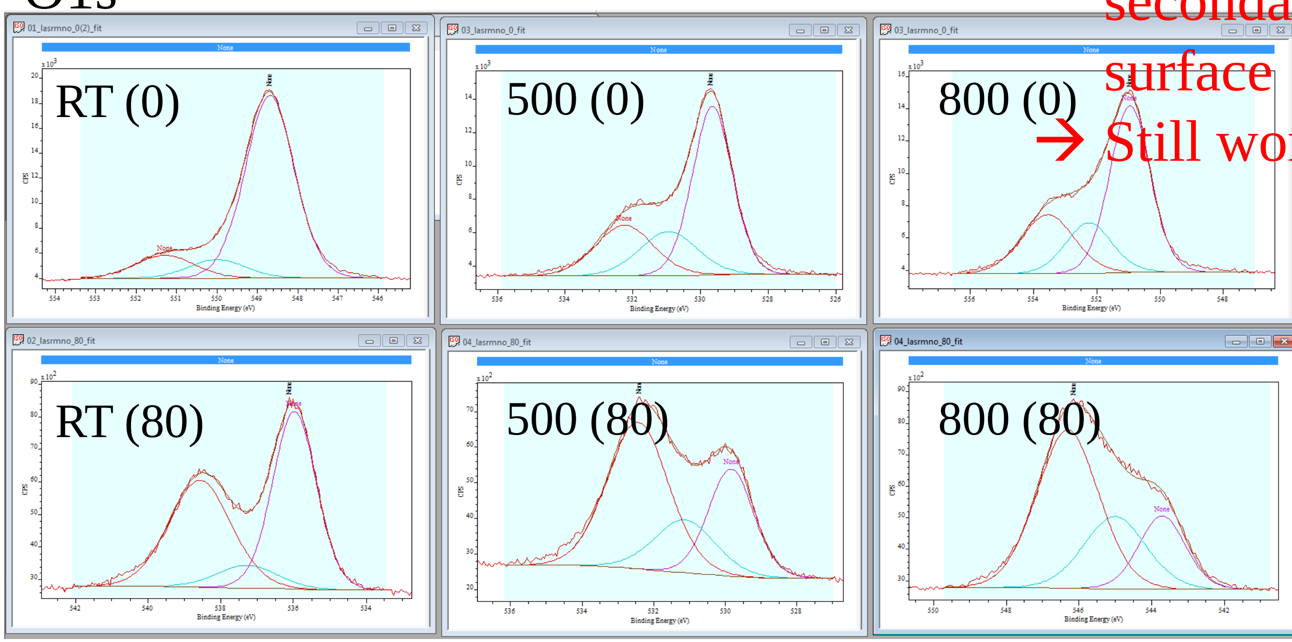


To extract more information from HR XPS, especially to identify the chemical composition of surface layer or secondary phase.

→ This can be useful to describe segregation before forming secondary phases on the surface

→ Still working on this analysis

O1s

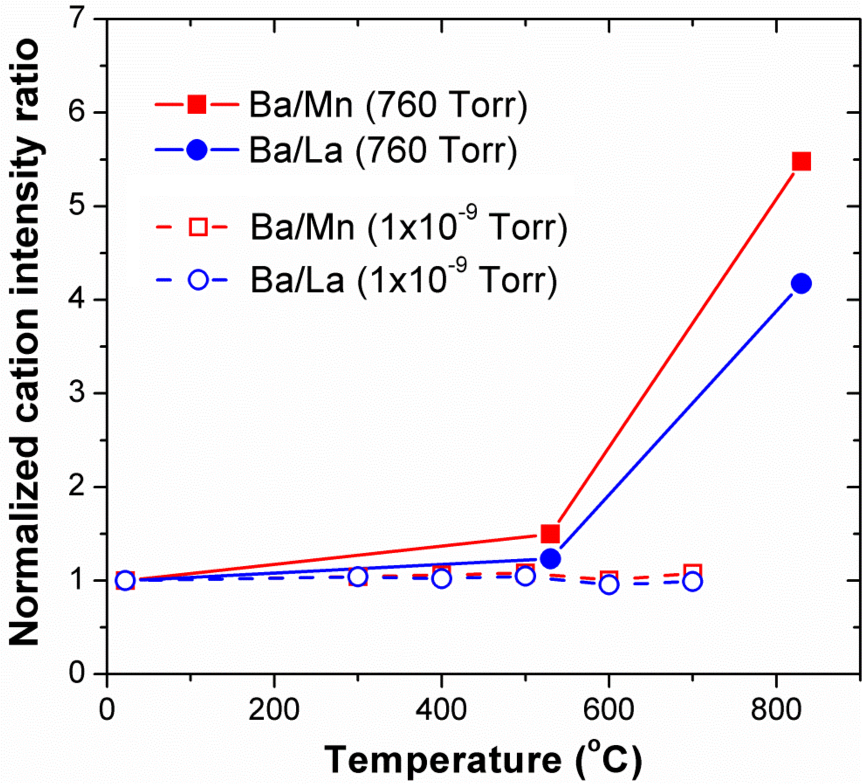


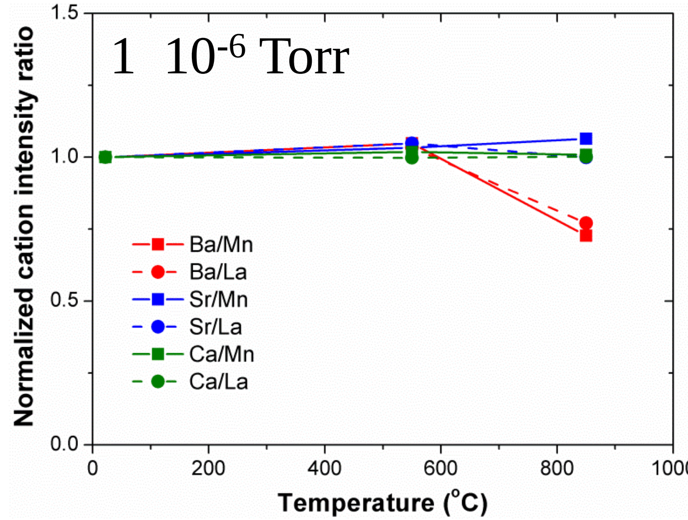
Effects of Vacancy Distribution on Dopant Segregation

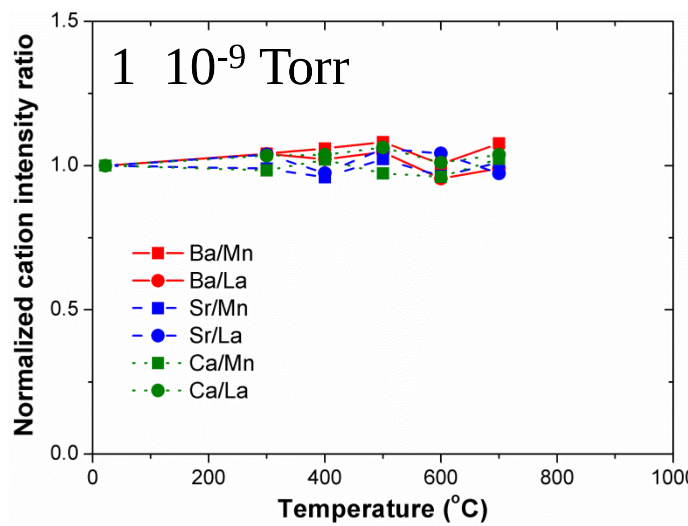
Other thoughts on this difference (high pO2 vs. low pO2)

If there is strong interaction between the oxygen vacancy (+) and cation vacancy (-), more oxygen vacancies on the surface in UHV would attract more cation vacancies on the surface. Then, it will be difficult for cations to diffuse towards the surface, and/or the cation vacancies will provide rooms for segregated cations?
But, we need to know the diffusivity of cations at 500-800C to see they are mobile enough

Effects of Oxygen Pressure on Dopant Segregation



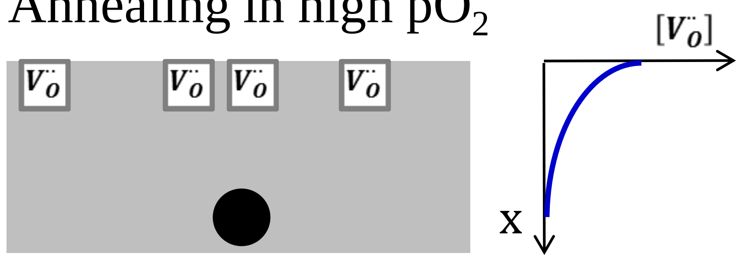




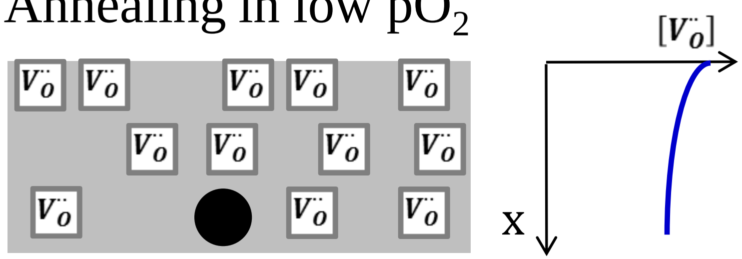
Cation intensity ratio using XPS (left) and AES (right)

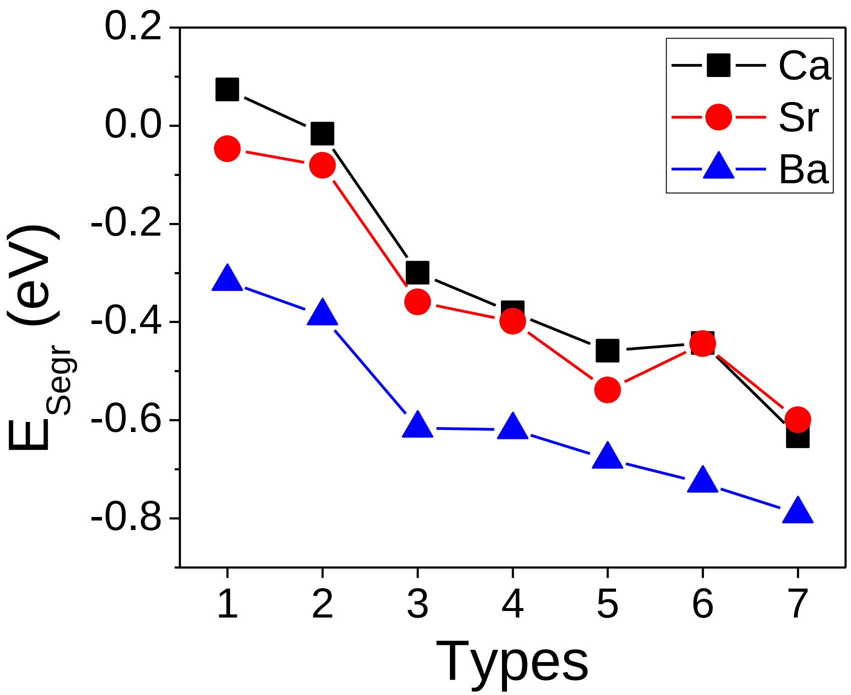
Effects of Vacancy Distribution on Dopant Segregation

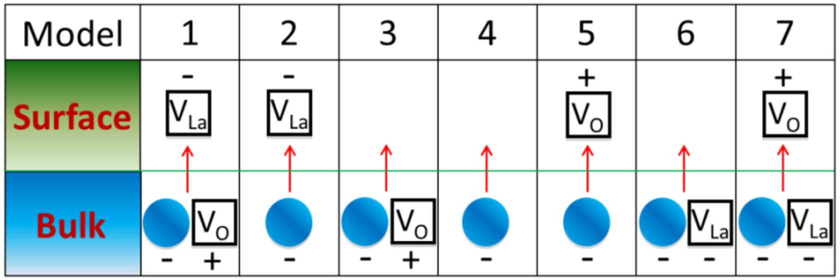
Annealing in high pO_2



Annealing in low pO_2







Elastic (dopant size mismatch) + Electrostatic (charged defects distribution)