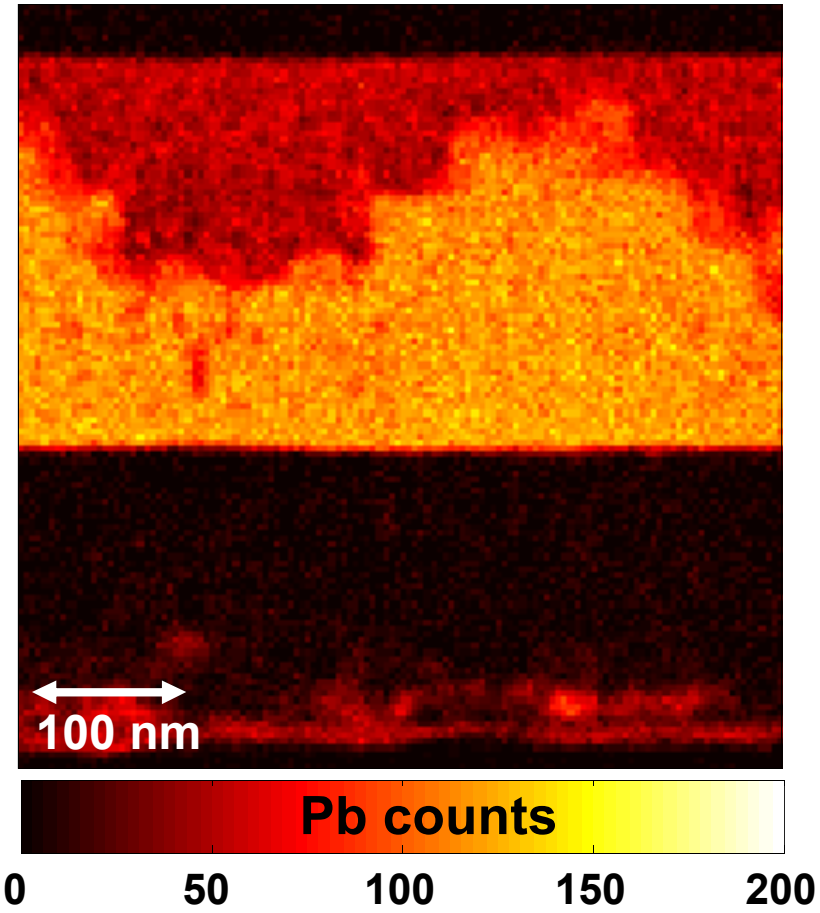
SAND2008-3713P

Quantitative X-ray spectrum imaging in $(Pb,La)(Zr,Ti)O_3$



Chad Parish

Collaborators:
Geoff Brennecka
Bruce Tuttle
Luke Brewer

Acknowledgements:
Michael Rye
Garry Bryant
Paul Kotula
Joe Michael

National Nuclear Security Administration

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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Thin-film P(L)ZT ferroelectrics are important for capacitor applications

$Pb(Zr,Ti)O_3$ and $(Pb,La)(Zr,Ti)O_3$:

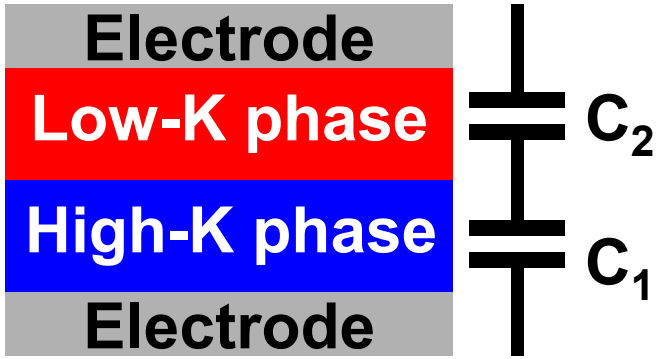
High-dielectric-constant (K) ferroelectrics for multilayer thin films

→Referred to as PZT and PLZT

Multiple phases can form during processing

Act as series capacitors

→ Loss of overall capacitance of device



$$C_{TOTAL} \propto \frac{1}{1/C_1 + 1/C_2}$$

Lowest capacitance value dominates device performance!

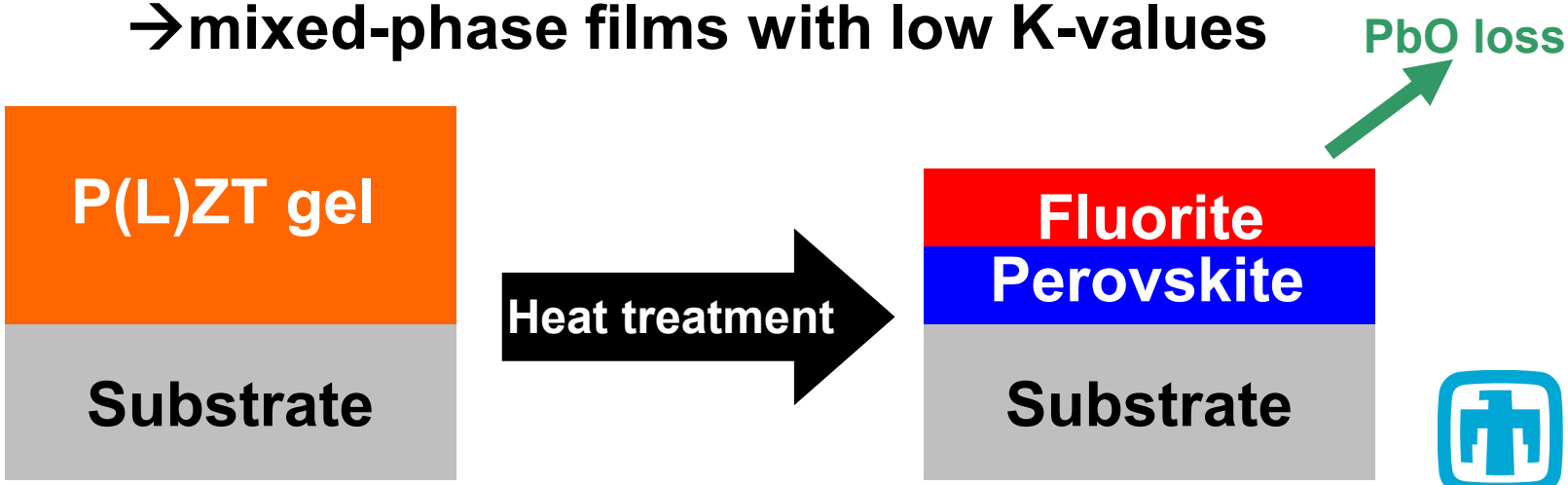
PbO volatility can result in poor film quality

Only the perovskite phase of P(L)ZT has high K

Perovskite is intolerant of Pb non-stoichiometry

When Pb-deficient, fluorite phase forms, with poor dielectric properties

PbO is volatile → lost during processing
→mixed-phase films with low K-values



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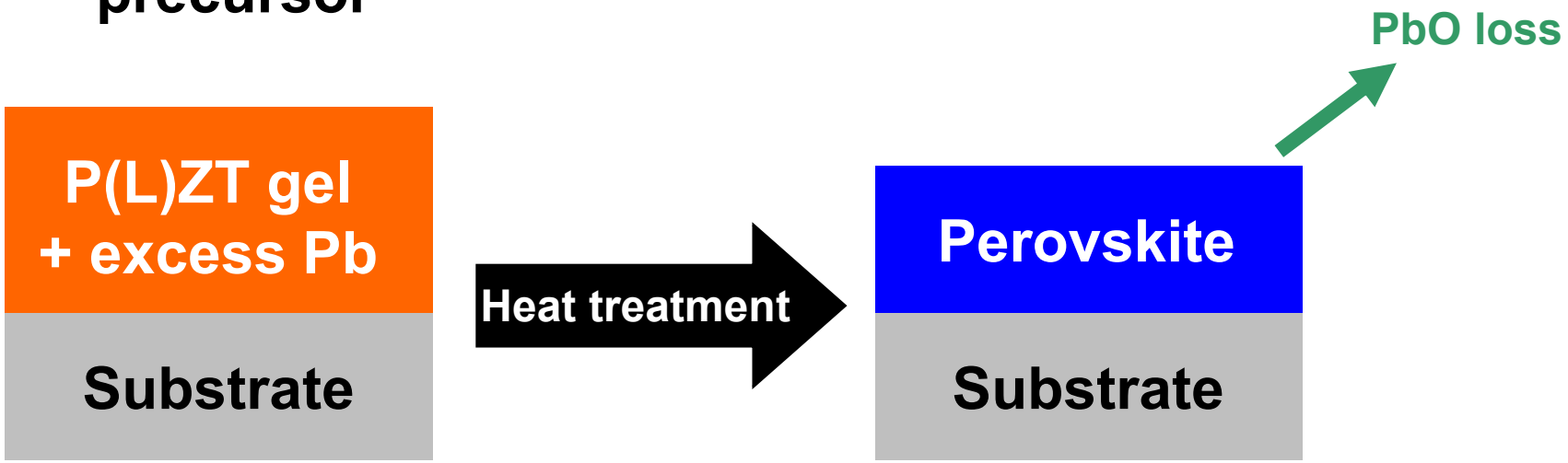
Excess Pb avoids fluorite formation, but has detrimental effects

Typically, 10+% excess Pb is added to the precursor



Thinner films require more Pb excess, which interacts with the electrode and substrate

Can we produce single-phase perovskite P(L)ZT <u>without</u> excess Pb?

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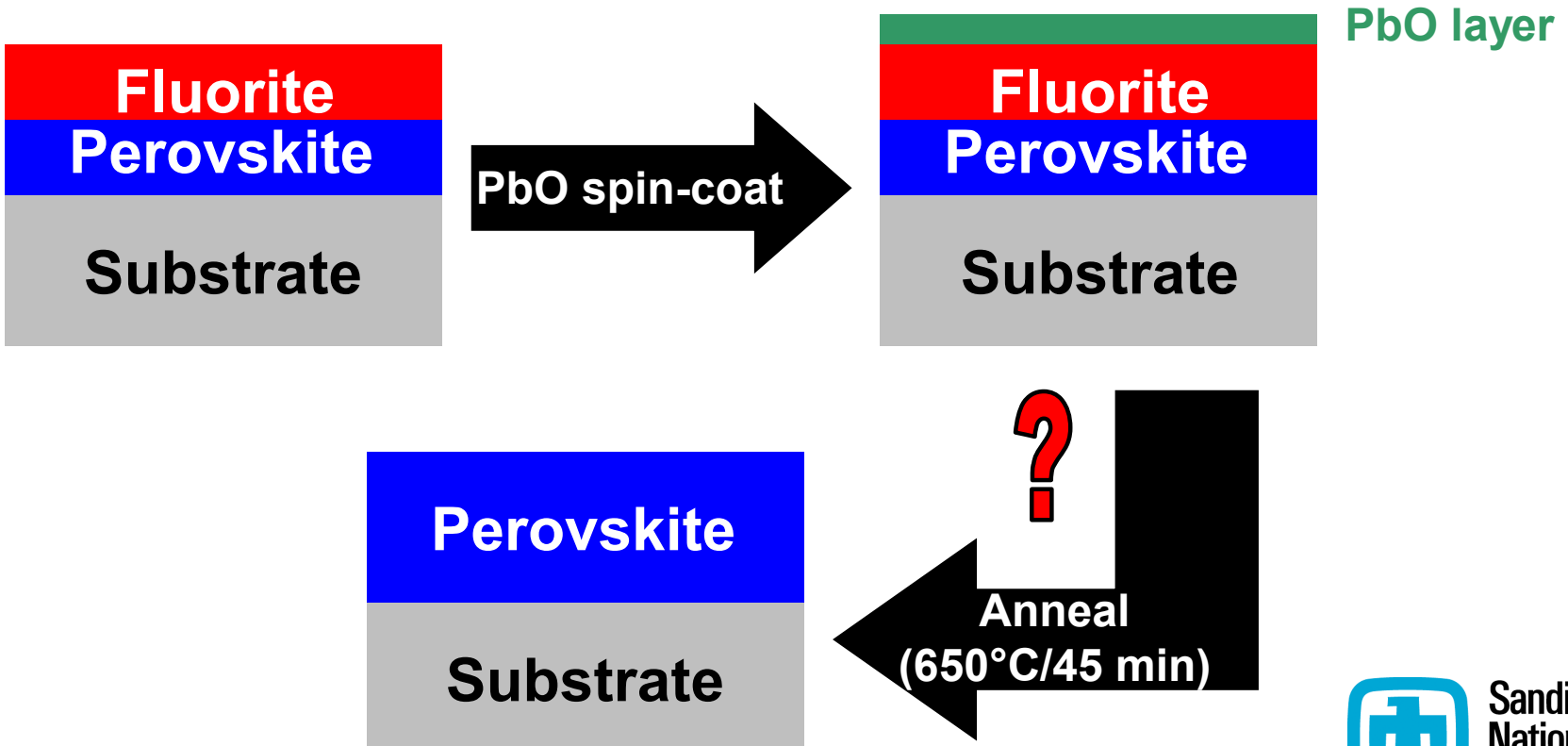
Will annealing crystallized films under a PbO solution restore the desired phase?

Hypothesis: ***If we coat mixed-phase perovskite + fluorite films with PbO solution and anneal, the fluorite will convert to the desired perovskite phase***



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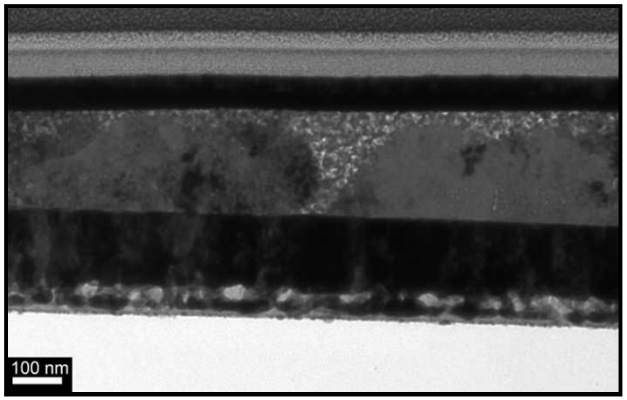
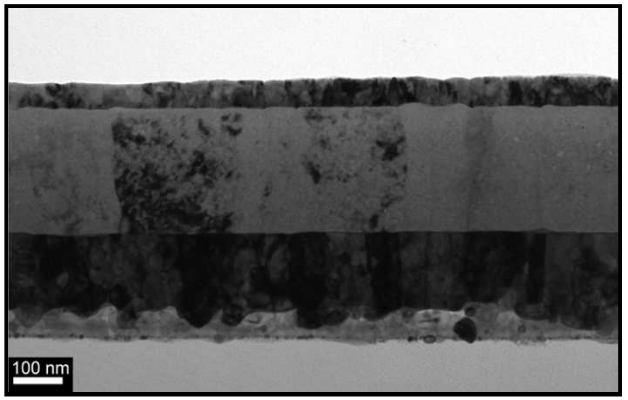
Microscopy shows mixed-phase structures converted to single-phase

Before overcoat+anneal

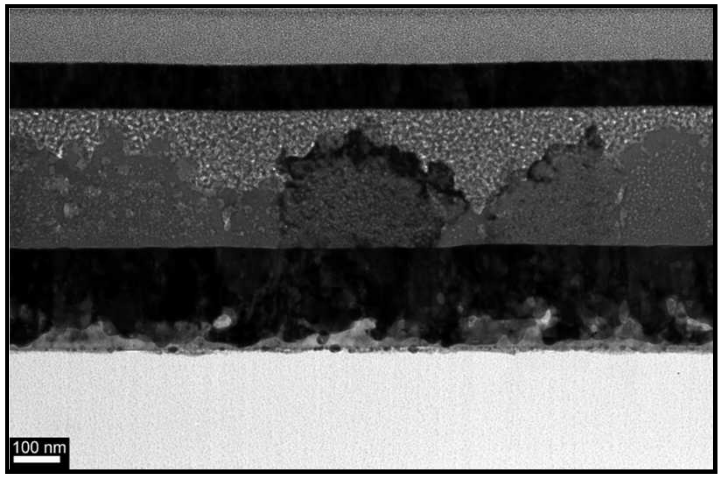
After overcoat+anneal

PZT 53/47





PLZT 12/70/30



FIB-Pt

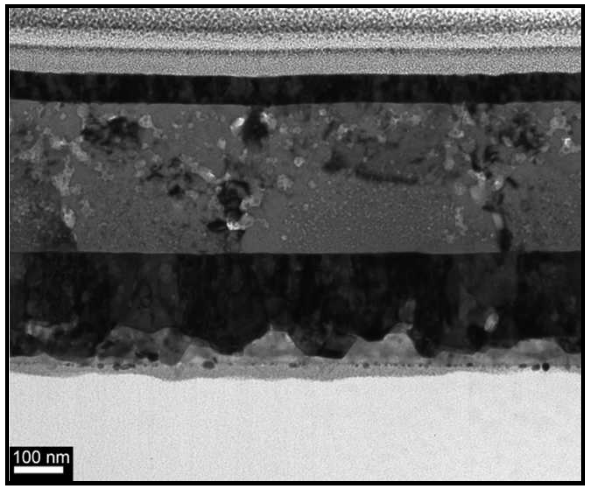
Pt

Film

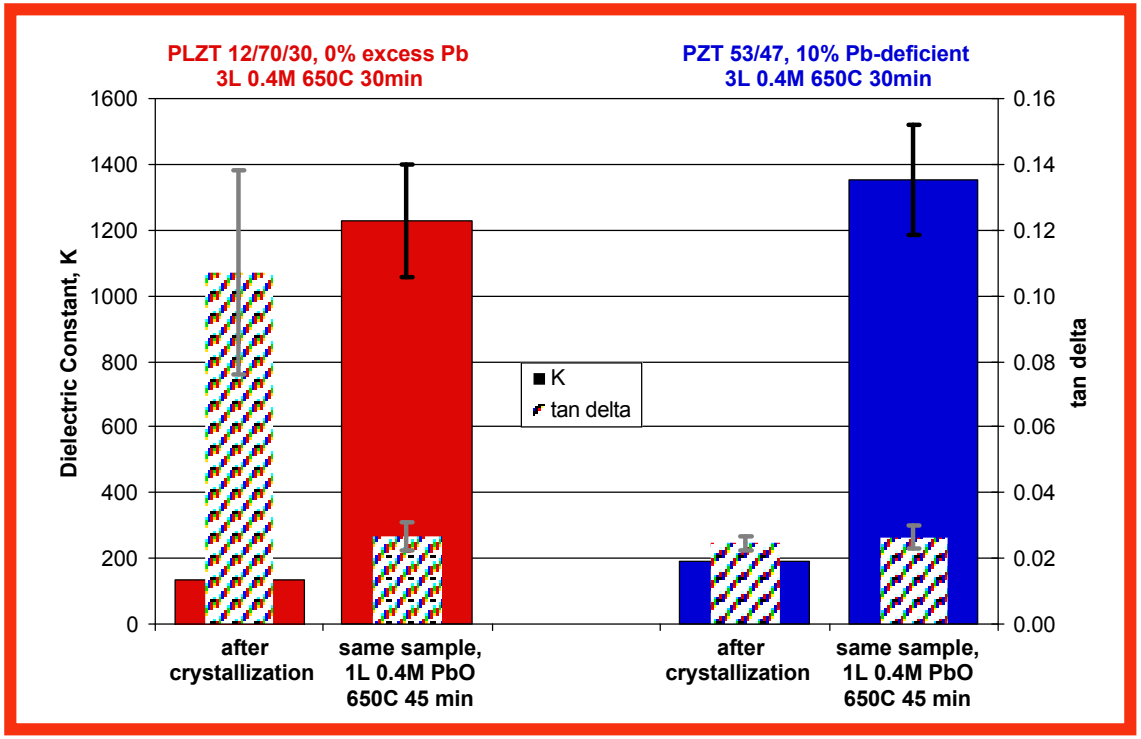
Pt

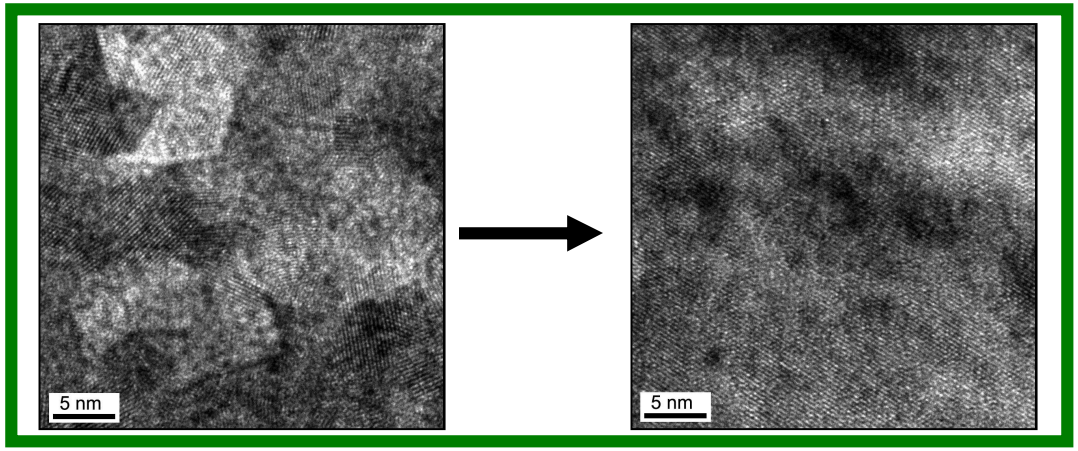
Ti

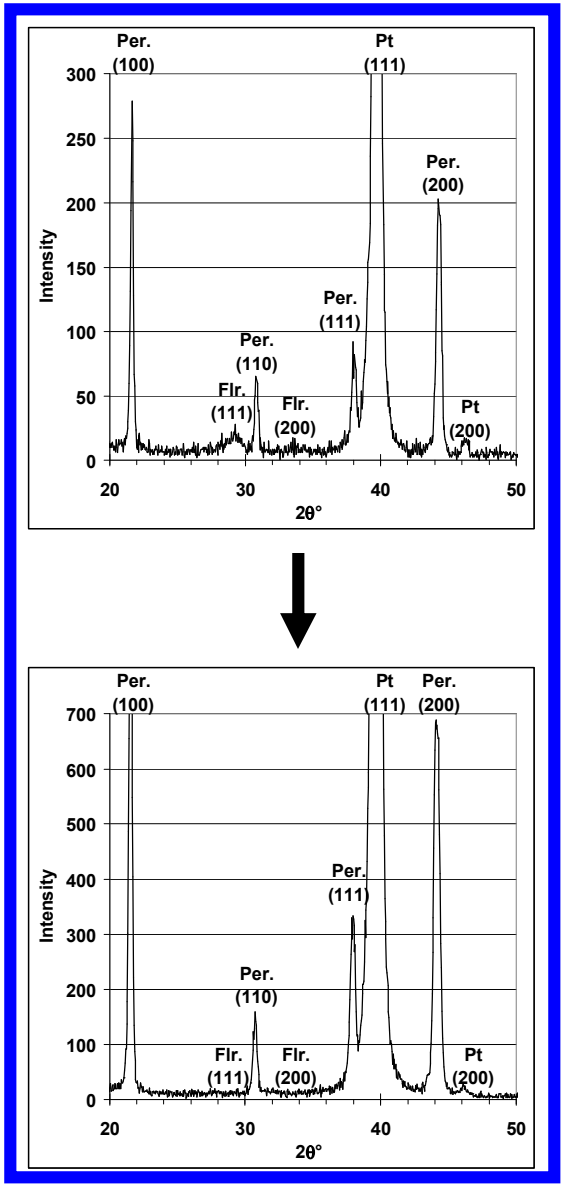
SiO_2



XRD, HREM, and electrical properties confirm the hypothesis







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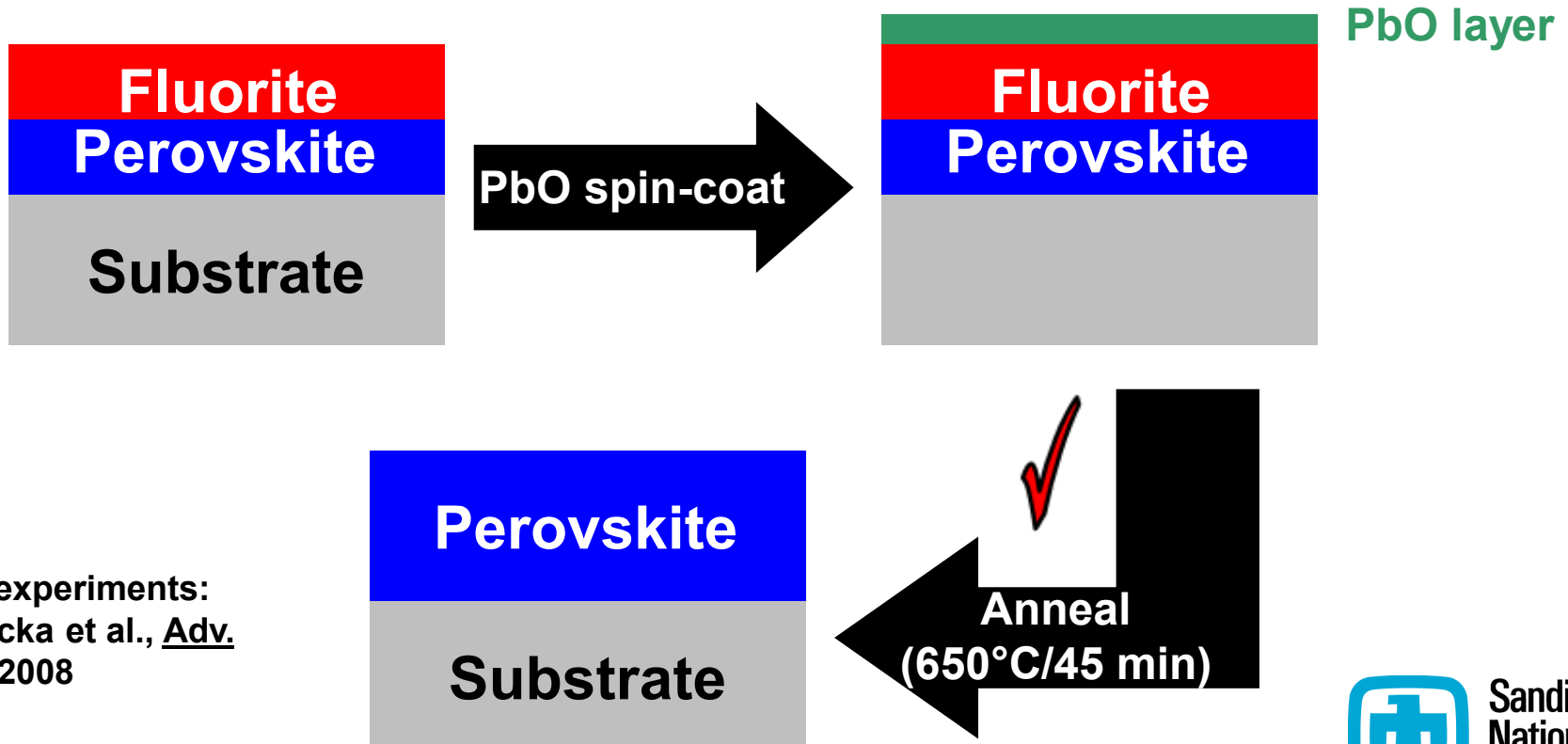

Above experiments: Brennecka et al., Adv. Mater., 2008

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We've characterized the structure – but what about the chemistry?

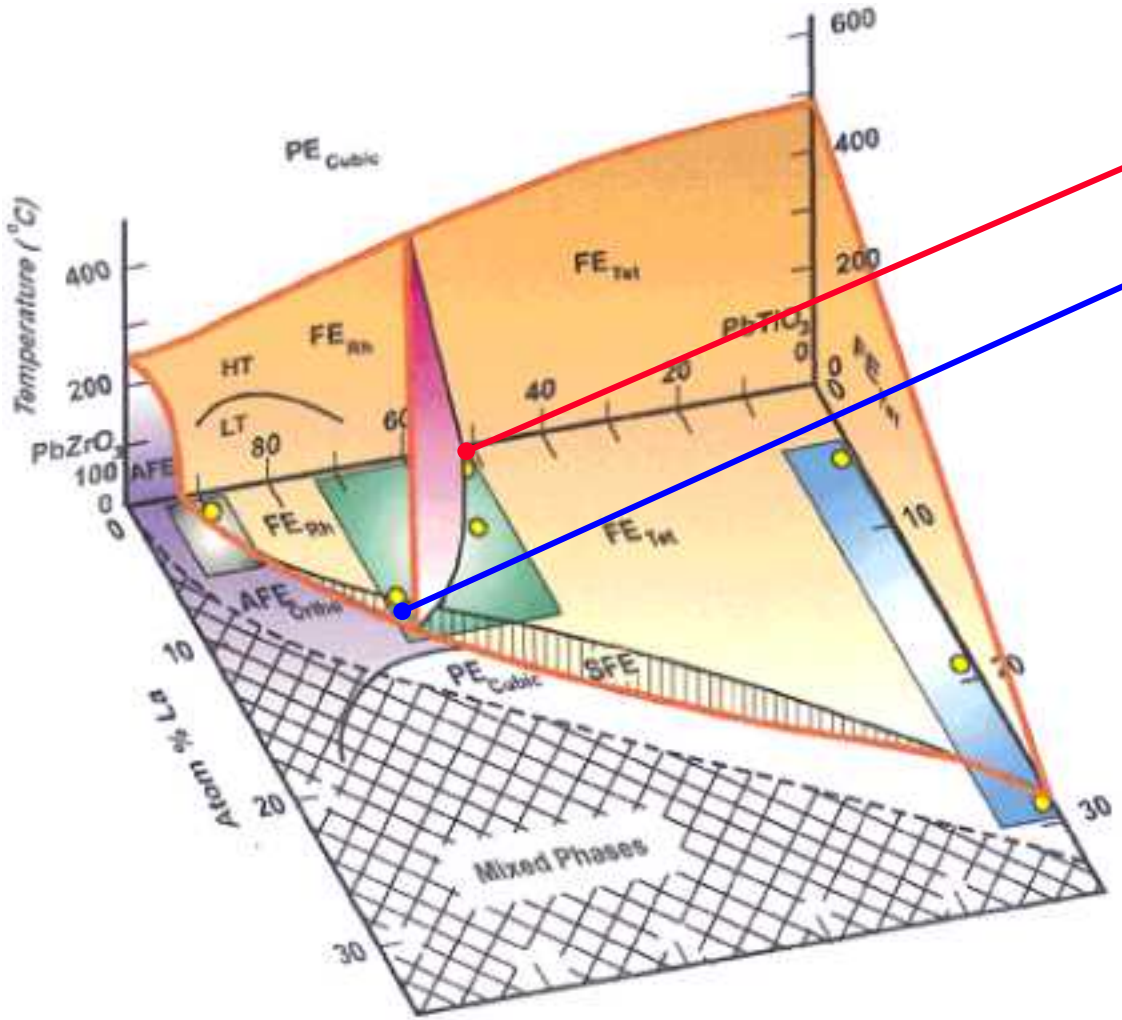
The previous experiments showed us the structural evolution

P(L)ZT film properties are sensitive to local chemistry

- Pb/B-site ratio
- Zr/Ti ratio
- La doping

→Can we use EDS in STEM to study this local chemistry?

Accurate measurement of cation content is important to interpret properties



PZT 53/47

PLZT 12/70/30

In general, best dielectric properties at phase boundaries

Haertling, J. Am. Ceram. Soc., V82, 1999, P.797

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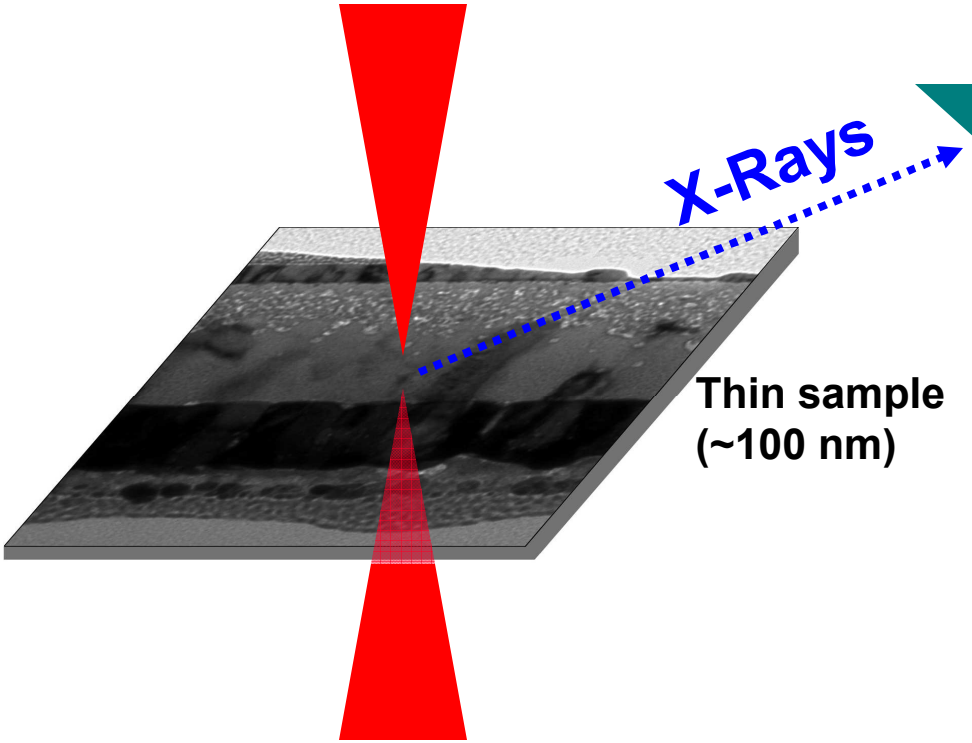
EDS allows us to qualitatively and quantitatively measure chemistry

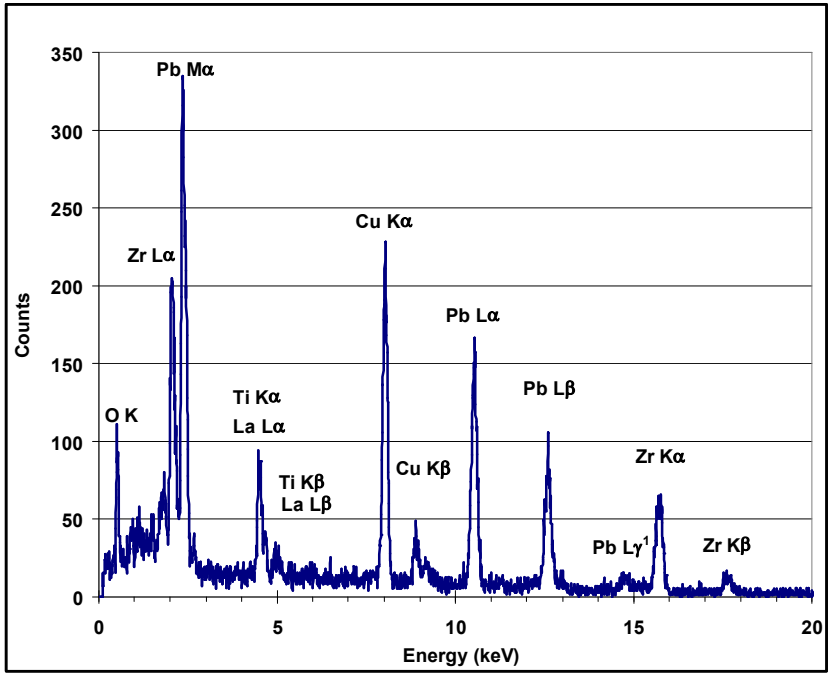
Scanning TEM (STEM) beam



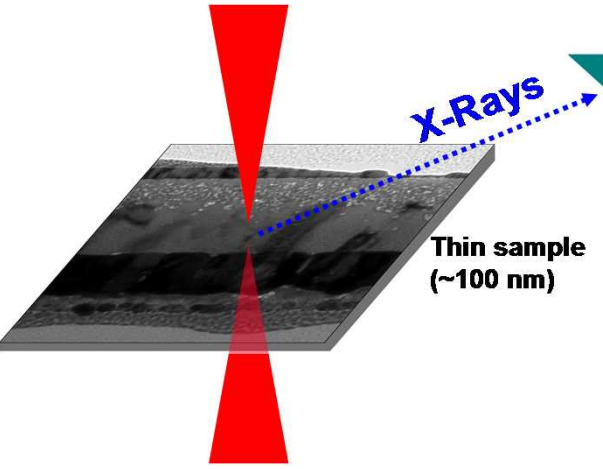
EDS: Energy-dispersive X-ray spectroscopy

EDS detector

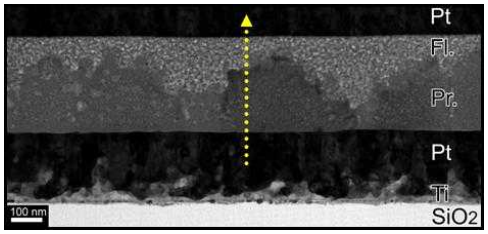
Data



Quantification of linescans time-consuming, but straightforward

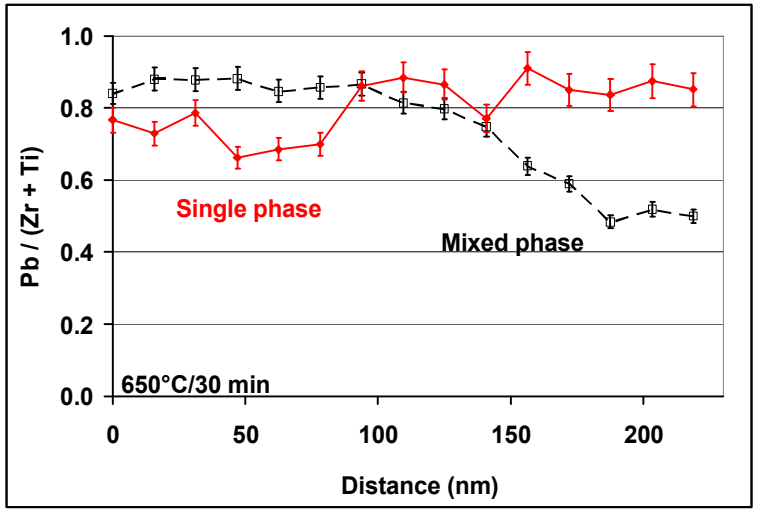


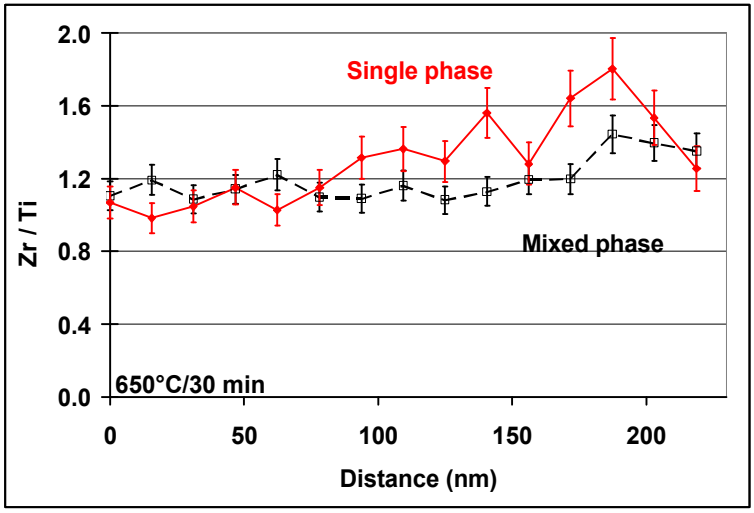
EDS detector



$$\frac{C_A}{C_B} = k_{AB}\frac{I_A}{I_B}$$

$$\Delta\left(\frac{C_A}{C_B}\right) = \frac{C_A}{C_B}\cdot\sqrt{\left(\frac{\Delta k_{AB}}{k_{AB}}\right)^2 + \left(\frac{\sqrt{I_A}}{I_A}\right)^2 + \left(\frac{\sqrt{I_B}}{I_B}\right)^2}$$



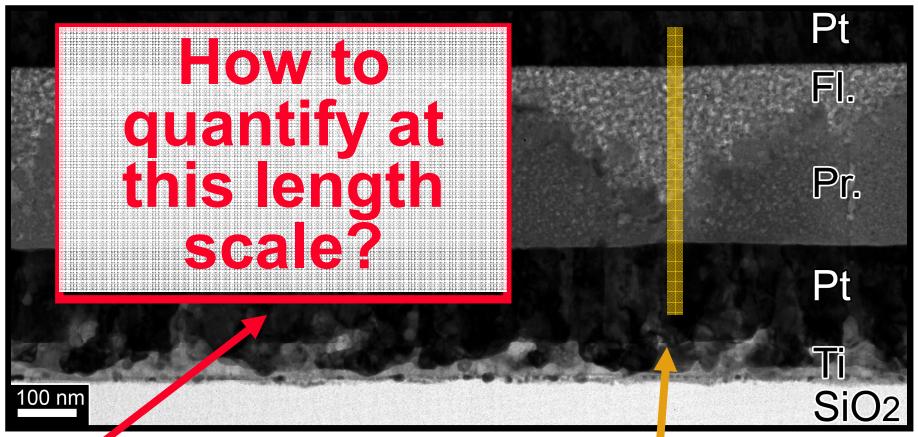


±3σ

Parish, Brennecka, Tuttle, and Brewer, J. Mater. Res., submitted

We need a technique to measure representative cation ratios

SIMS, XPS, AES depth profiling
~several 10s of μm
≠ feature size



Feature size
~hundreds of nms

EDS linescan sampling
<10 nm
≠ feature size

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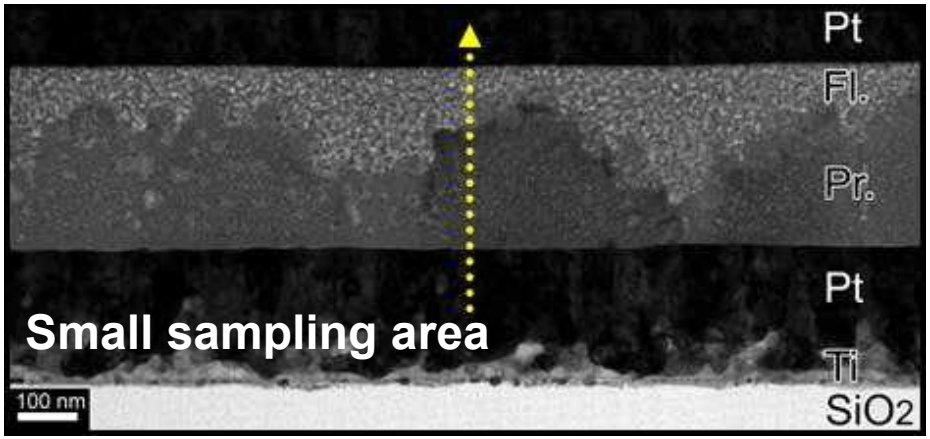
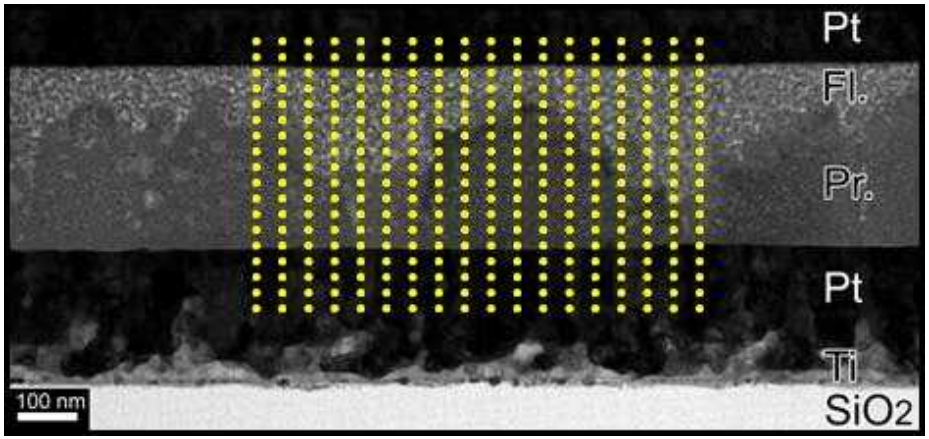
Comparisons: linescans and spectrum images (SIs)

EDS linescans



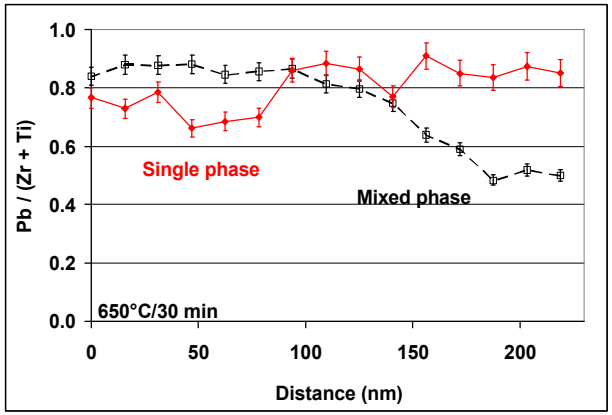
EDS SIs



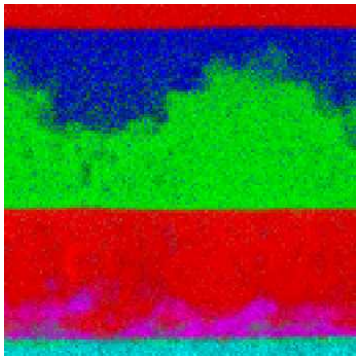
Quantification established in the literature

$$\frac{C_A}{C_B} = k_{AB}\frac{I_A}{I_B}$$

$$\Delta\left(\frac{C_A}{C_B}\right) = \frac{C_A}{C_B}\cdot\sqrt{\left(\frac{\Delta k_{AB}}{k_{AB}}\right)^2 + \left(\frac{\sqrt{I_A}}{I_A}\right)^2 + \left(\frac{\sqrt{I_B}}{I_B}\right)^2}$$



Qualitative analysis we understand, but how to quantify?



?

$C_{Pb} \pm \Delta Pb$

$C_{Zr} \pm \Delta Zr$

$C_{Ti} \pm \Delta Ti$

$C_{La} \pm \Delta La$

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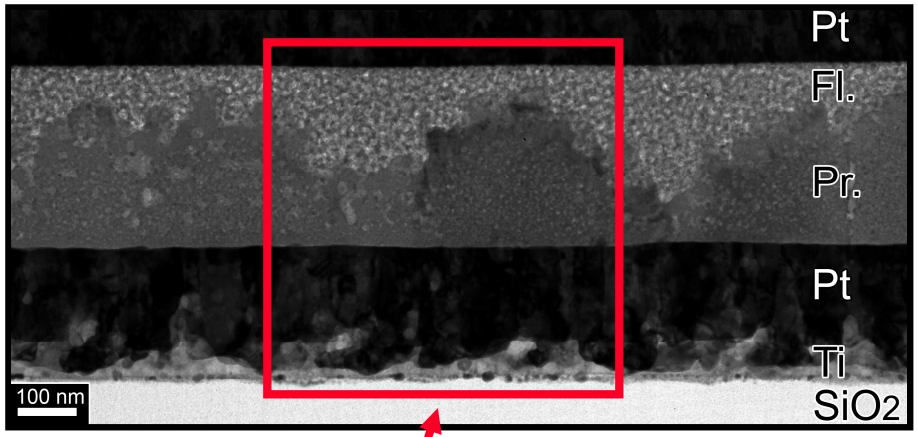
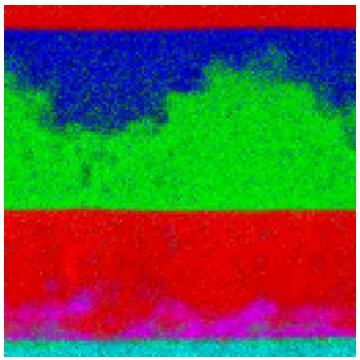
Can we use spectrum imaging?





?

$C_{Pb} \pm \Delta Pb$
$C_{Zr} \pm \Delta Zr$
$C_{Ti} \pm \Delta Ti$
$C_{La} \pm \Delta La$

Feature size ⇔ SI size

Spectrum imaging has the right length scale, but:

- **How to get cation fractions C_{Pb}, C_{Zr},…?** } Some literature available
- **How to get statistical uncertainties Δ?** } Unable to find any literature

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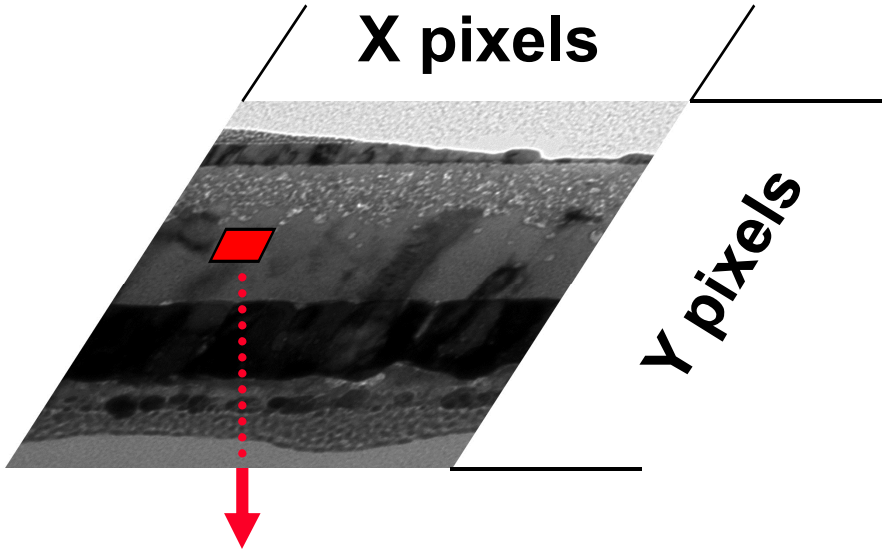
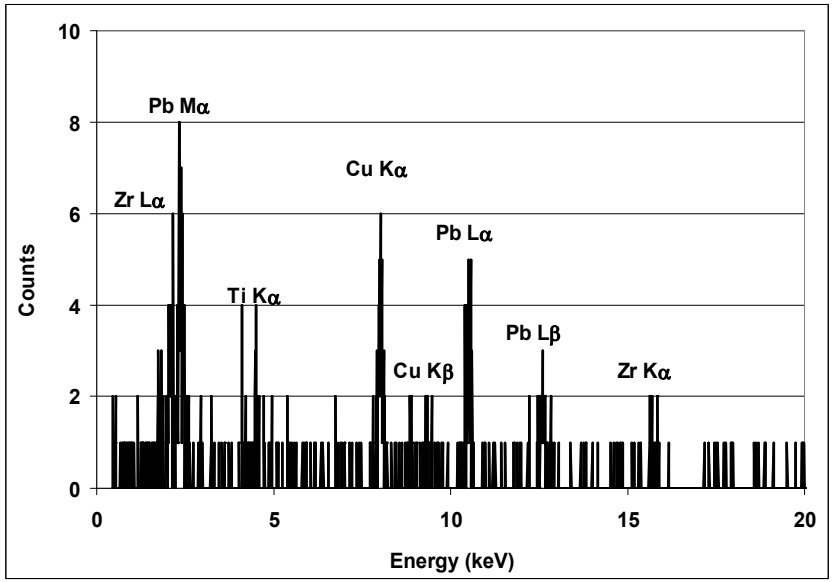
Spectrum imaging – need to mine the data





Typical dataset:

128×128 pixels

2048 channels/pix

∴34 million datapoints

How to make use of this?

→Multivariate Statistical Analysis (MSA)

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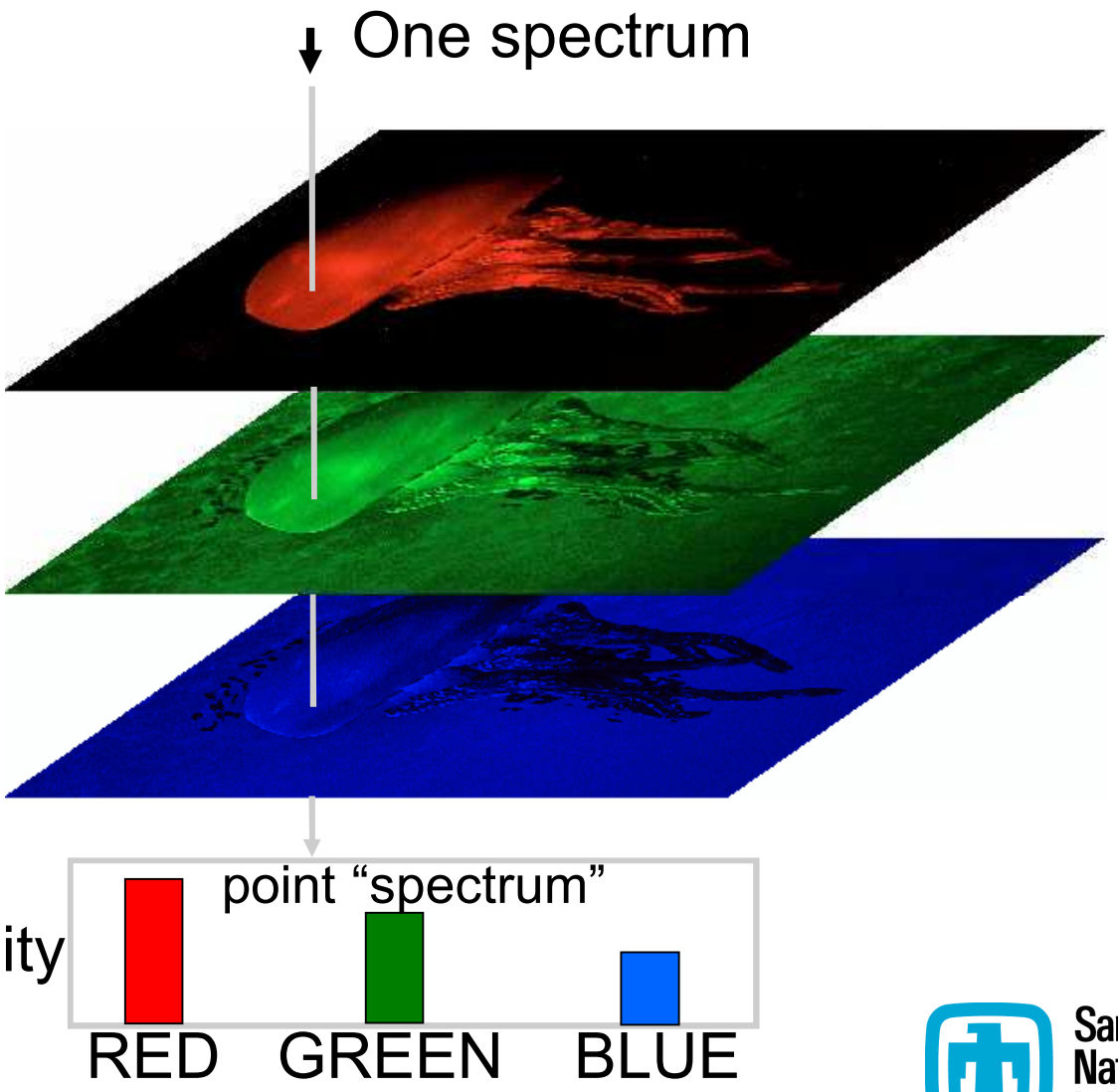
Color image: an example of a 3-channel spectrum image



(Slide courtesy M. Keenan and P. Kotula)

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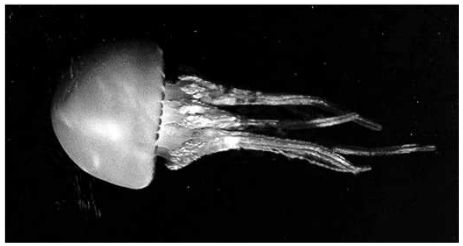
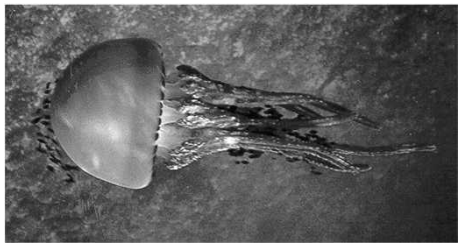
Spectrum image = (Concentration) · (Spectral component)^T

=



x

+



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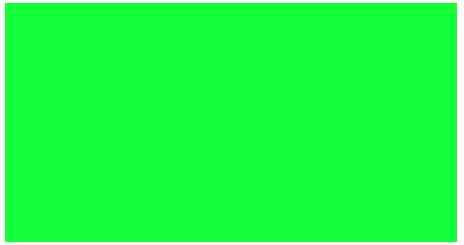

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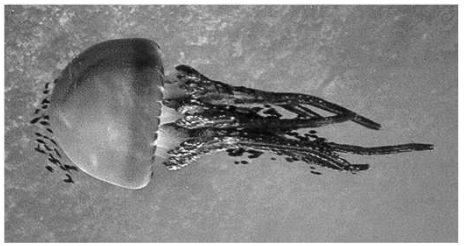
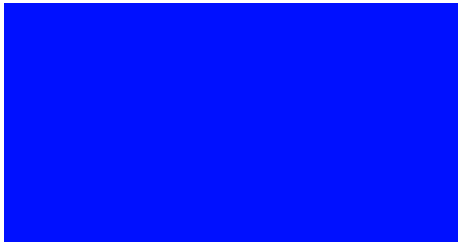


x



note the linearity assumption

(Slide courtesy M. Keenan and P. Kotula)

MSA finds the most relevant variations in the data

Original data ≈ Processed spectral image = Score images x (Loading spectra)^T

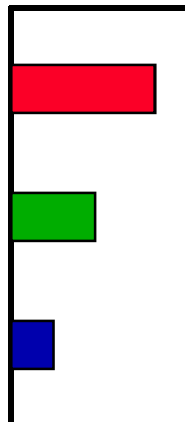
Original image

≈

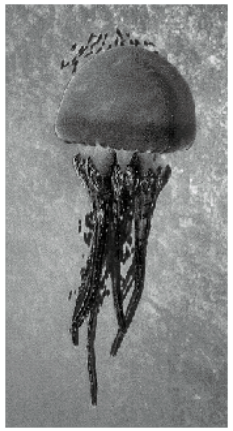
2-component model of color image

=

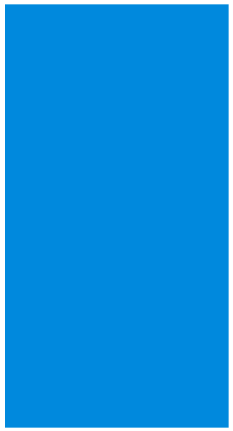
x

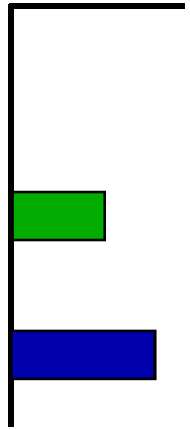


+



x





(Slide courtesy M. Keenan and P. Kotula)

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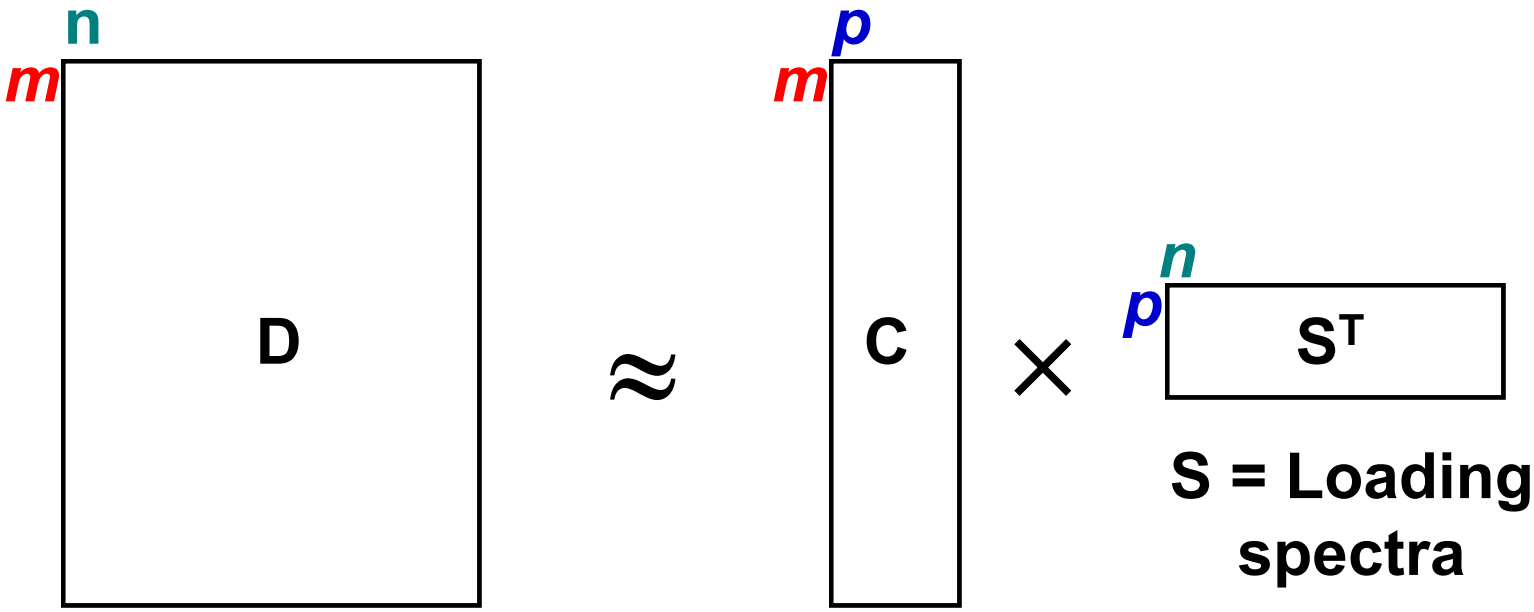
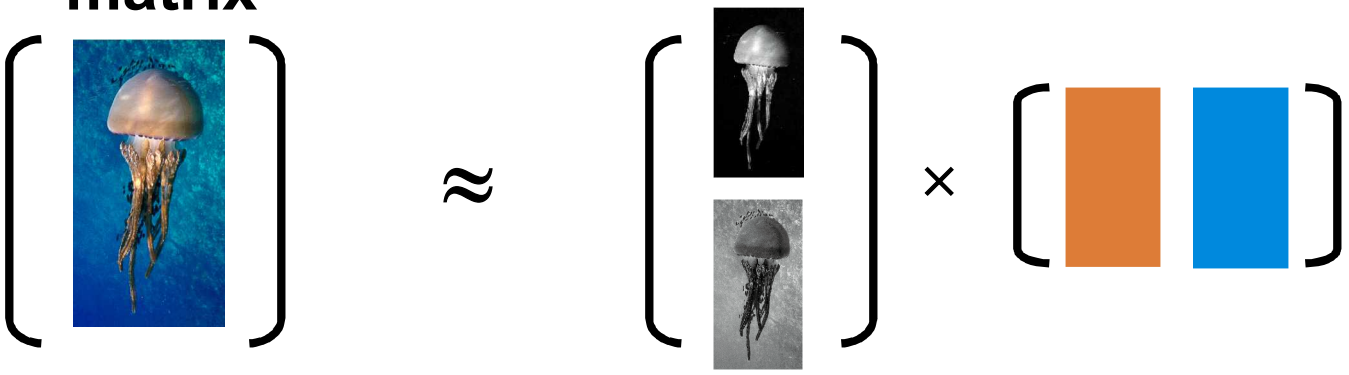


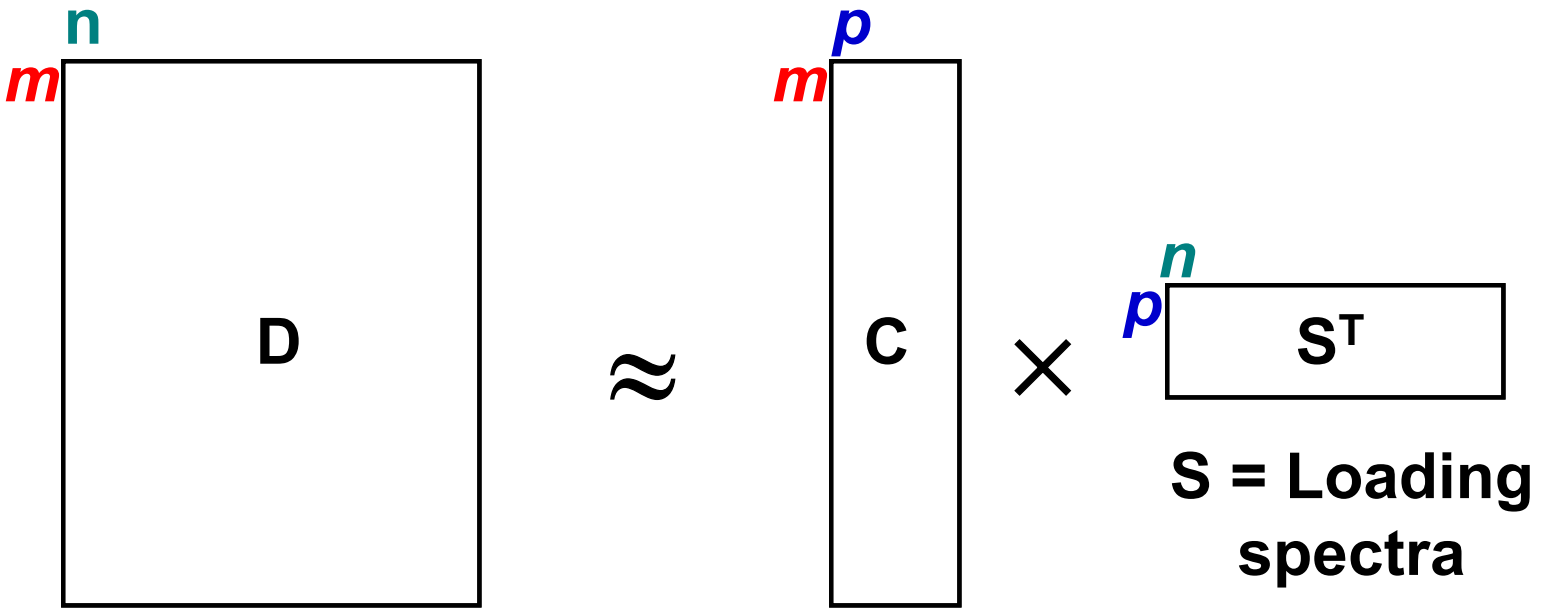
S = Loading spectra

D = Unfolded spectral image matrix

C =Score images



Principal Component Analysis (PCA) used to analyze our EDS spectrum images



S = Loading spectra

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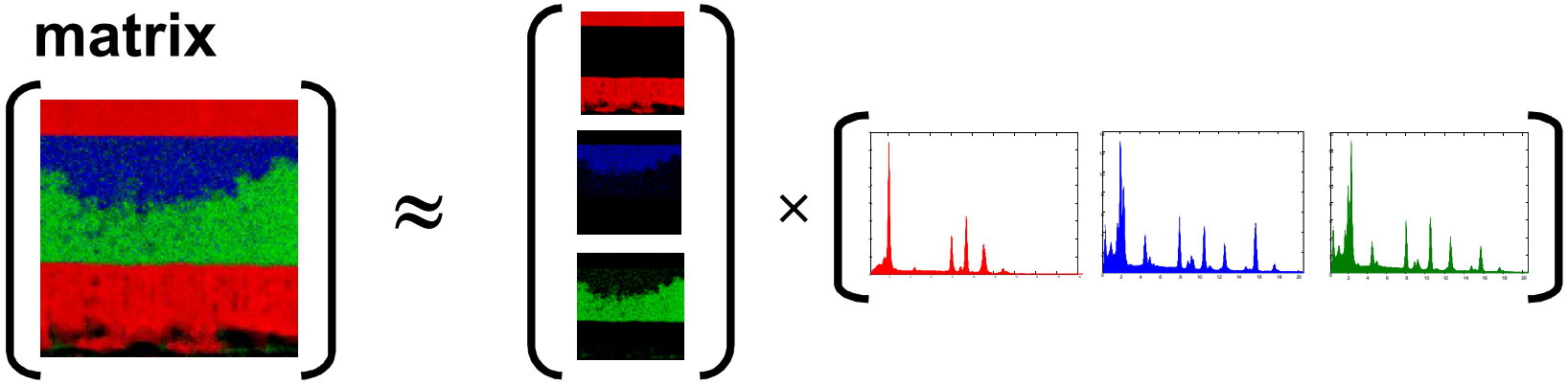
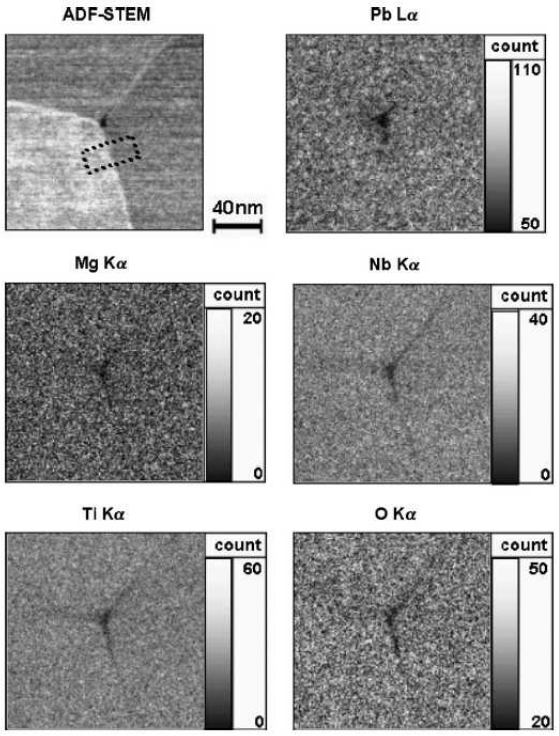
C =Score images



Pt
Fluorite
Perovskite

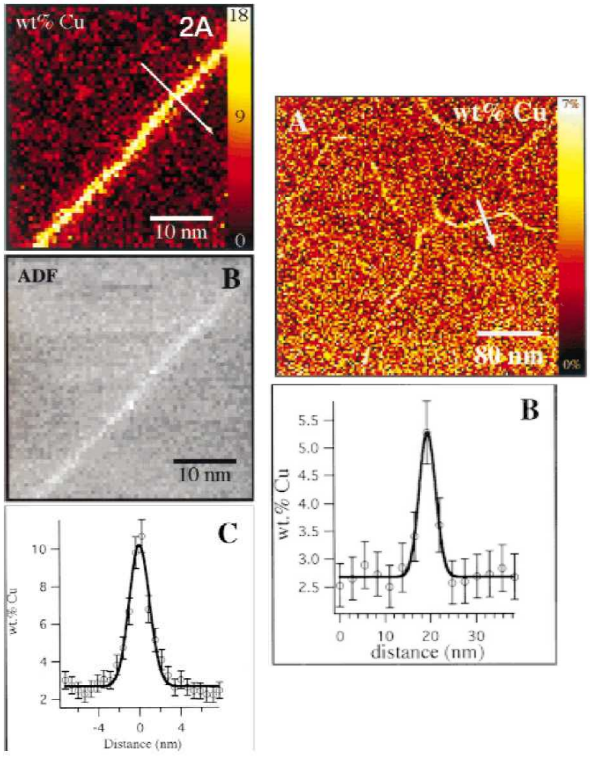
Many papers have quantified from dot maps or SIs (without MSA)

$Pb(Mg,Nb)O_3$-$PbTiO_3$



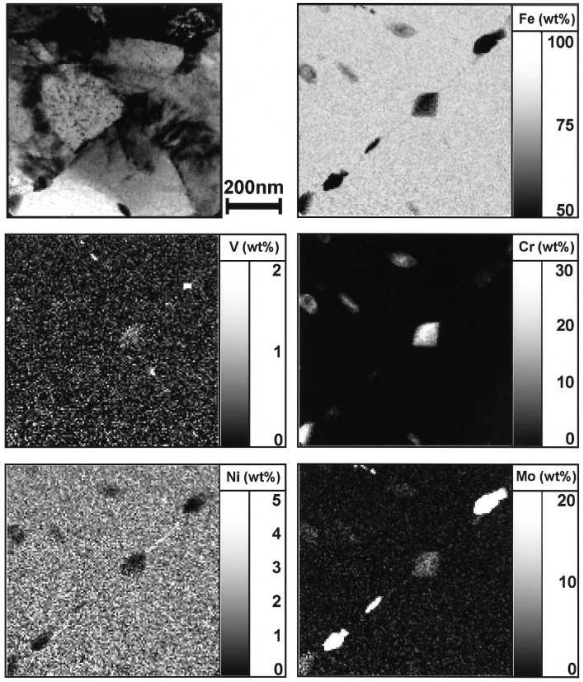
•Gorzkowski et al., J. Mat. Sci., V39, P.6735 (2004)
•(Lehigh Univ. VG STEM)

Al-4% Cu



•Carpenter et al., M&M, V5, P.254 (1999)
•(Lehigh Univ. VG STEM)

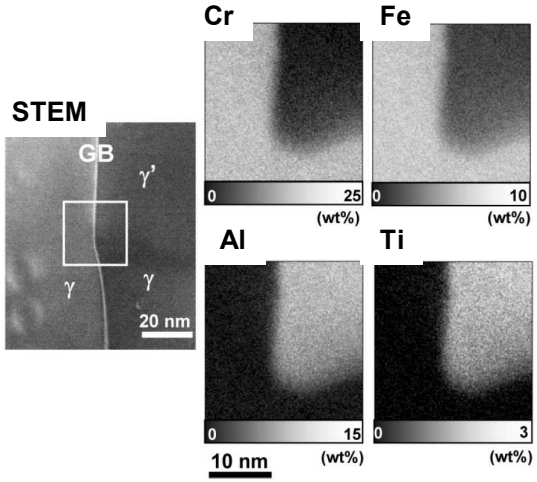
Prior-austenite grain boundary in steel

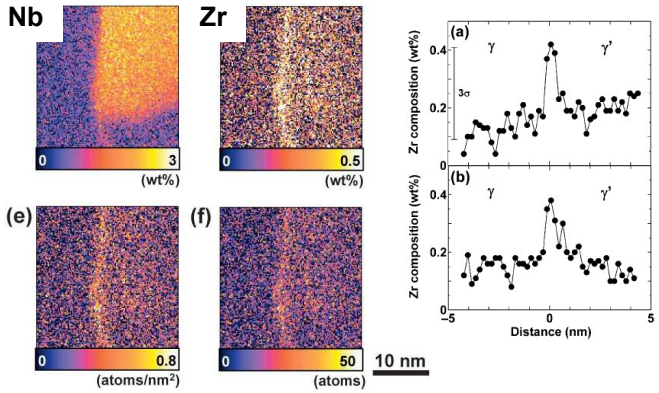


•Williams et al., J. Elec. Micros., V51(Supp.), P. S113 (2002)
•(Lehigh Univ. VG STEM)

A few papers have quantified with MSA

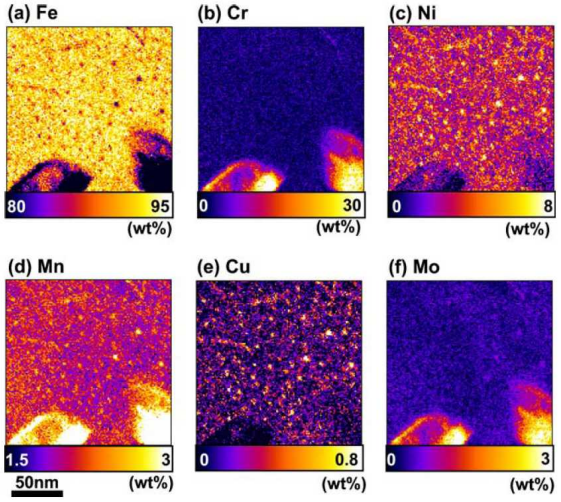
Ni-based superalloy





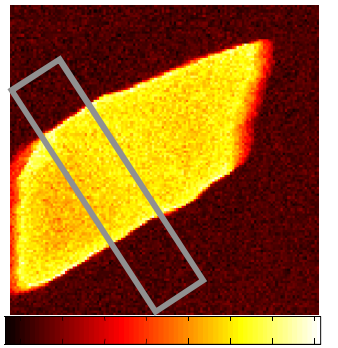
•Watanabe et al., M&M, V12, P.515 (2006)
•Lehigh Univ. VG STEM *(C_s corrected)*

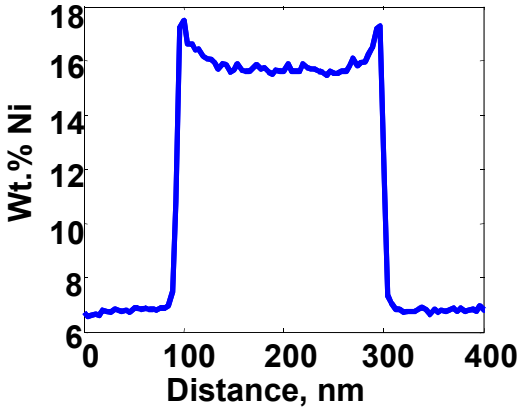
Irradiated alloy steel



•Burke et al., J. Mat. Sci., V41, P.4512 (2006)
•Lehigh Univ. VG STEM

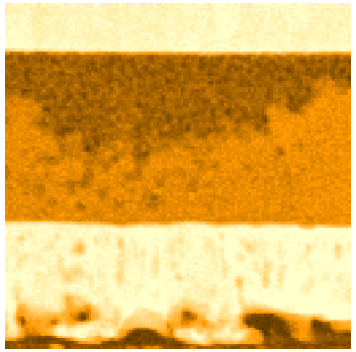
Fe-Ni meteorite

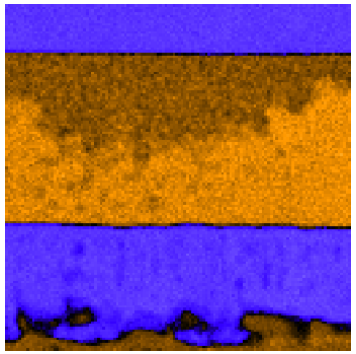


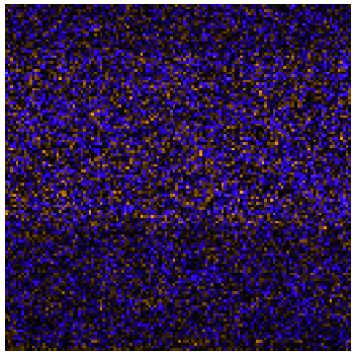


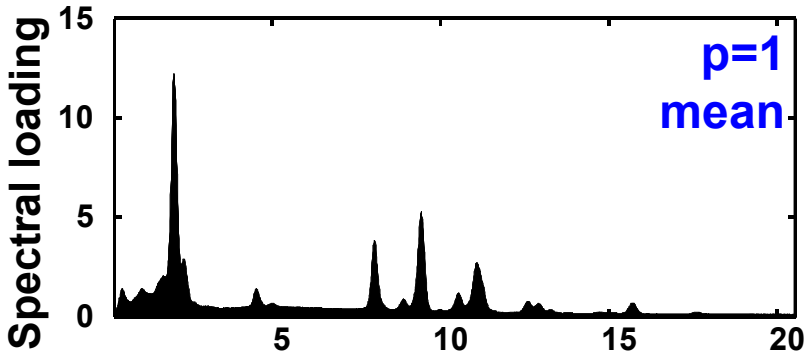
•Goldstein et al., Meteoritics & Planetary Sci., V42, P.913 (2007)
•Sandia Labs Tecnai TEM/STEM

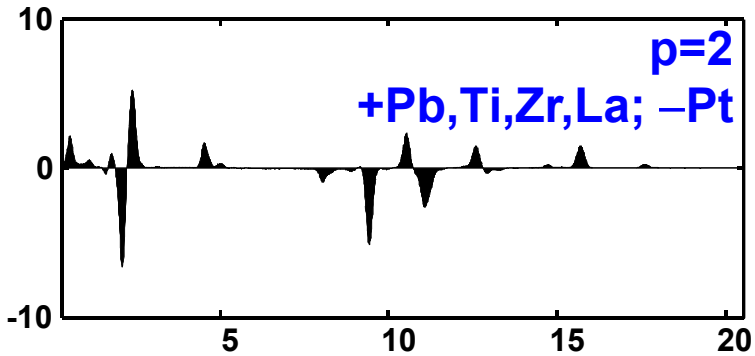
PCA finds the chemically relevant variations and rejects noise

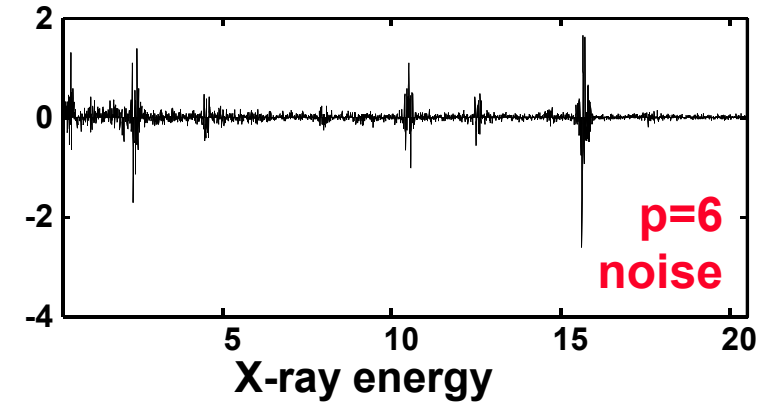


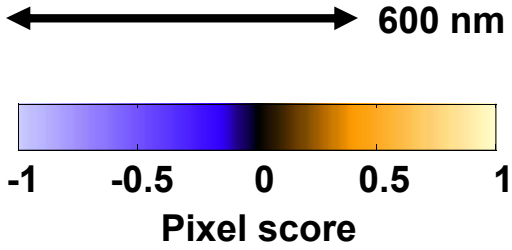


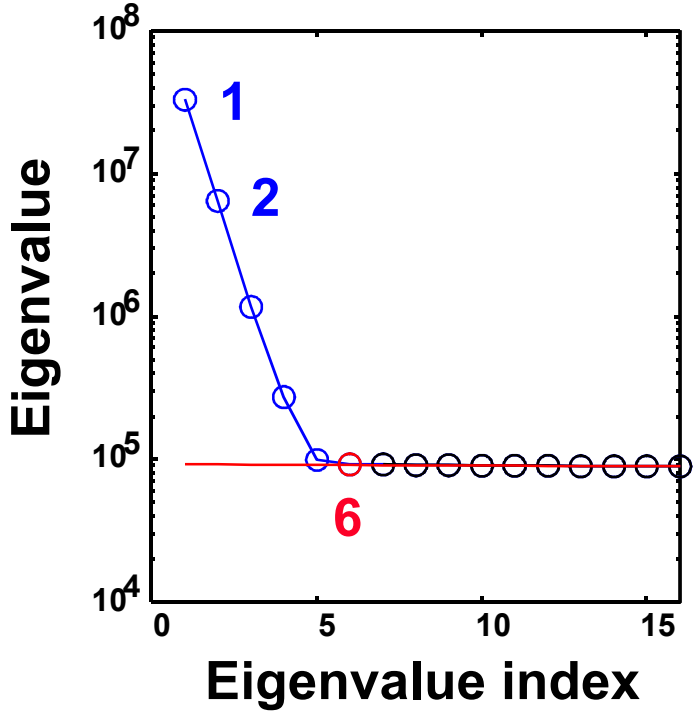












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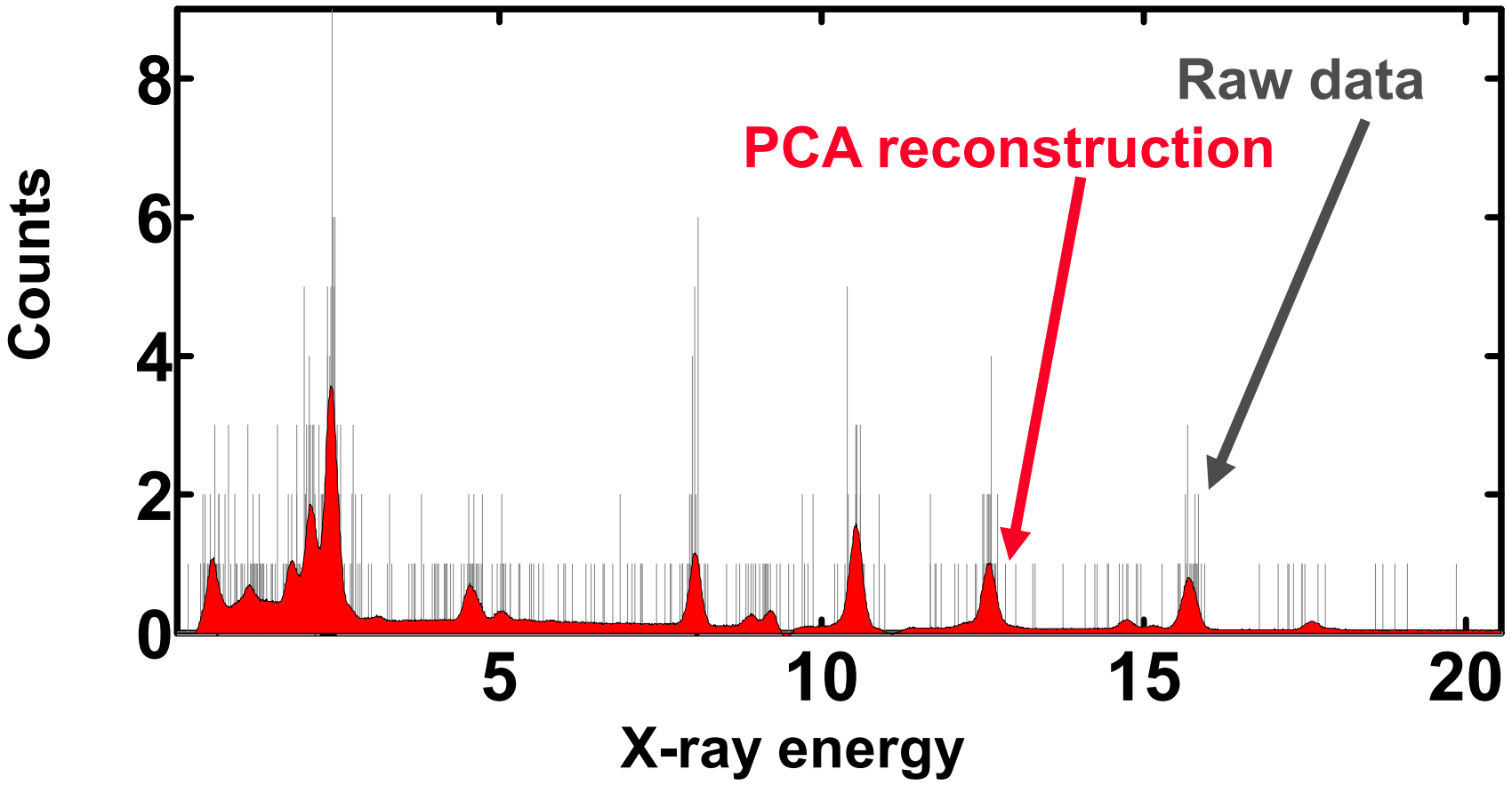
PCA produces a noise-filtered reconstruction of the data at every pixel



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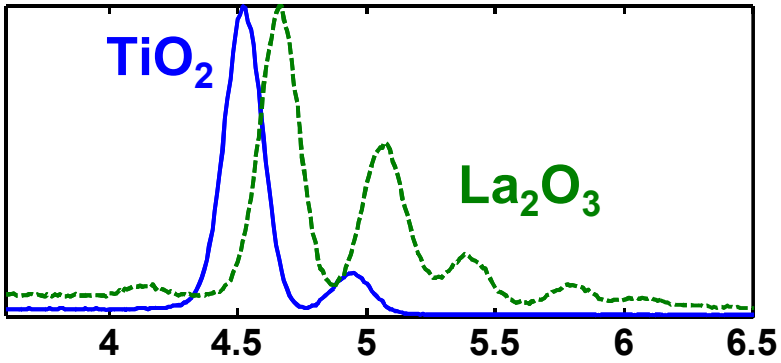
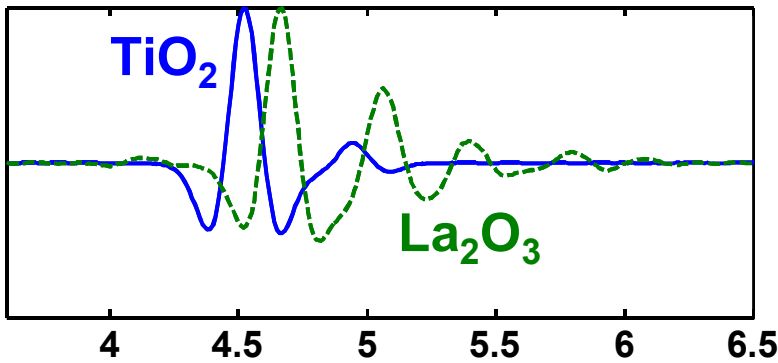
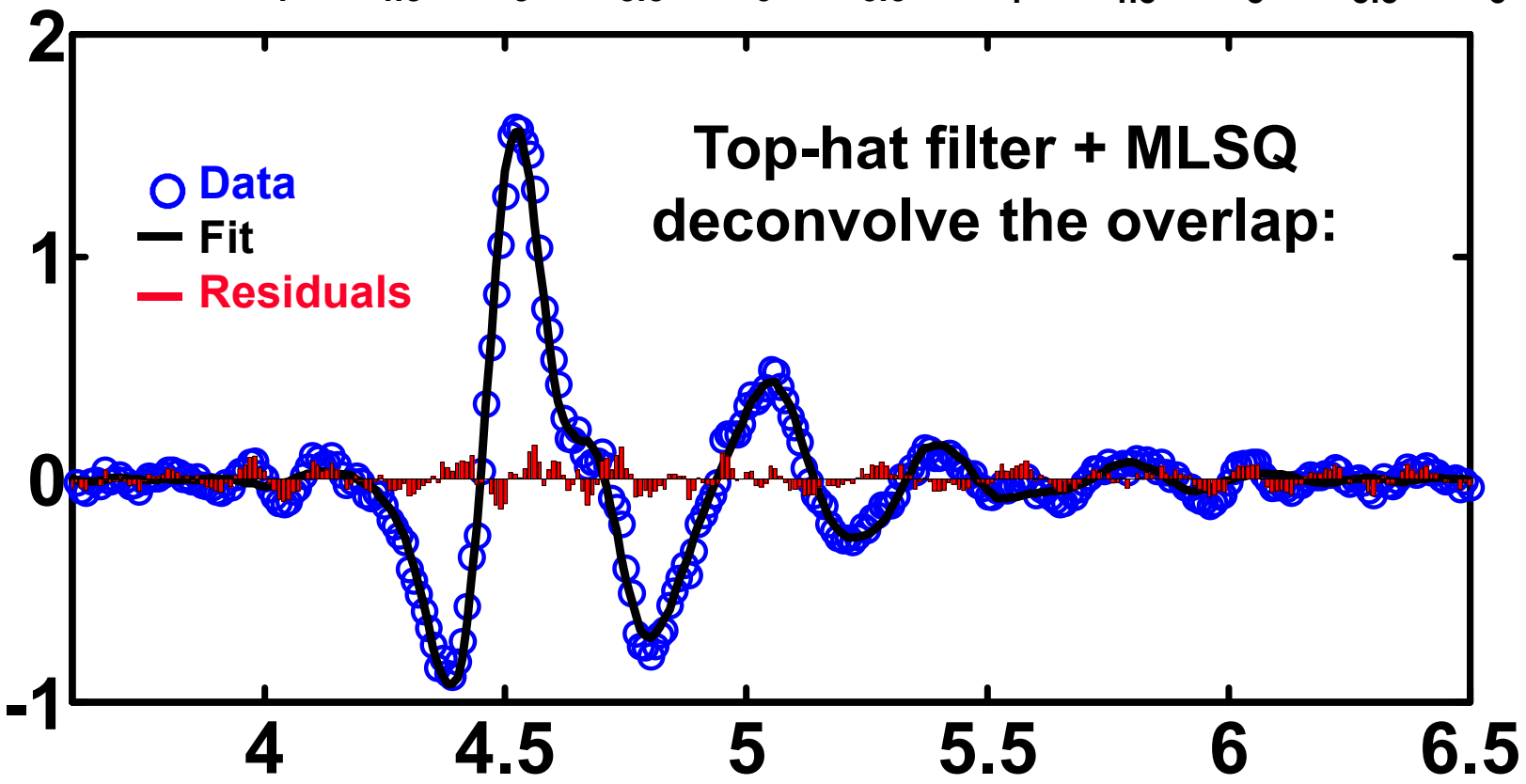
Noise-filtered spectra can be deconvolved and integrated

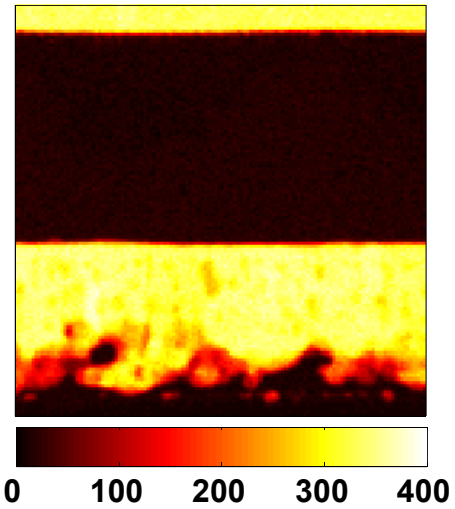
Ti K and La L lines overlap:



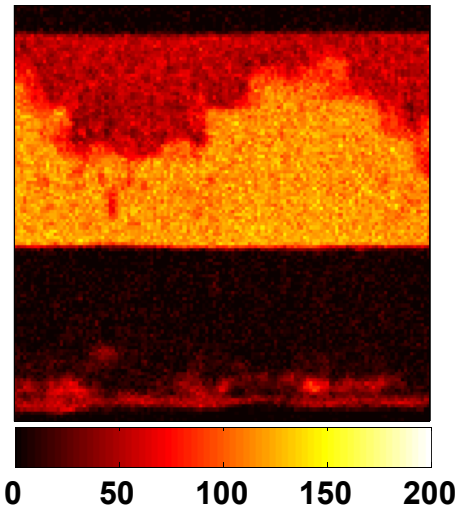




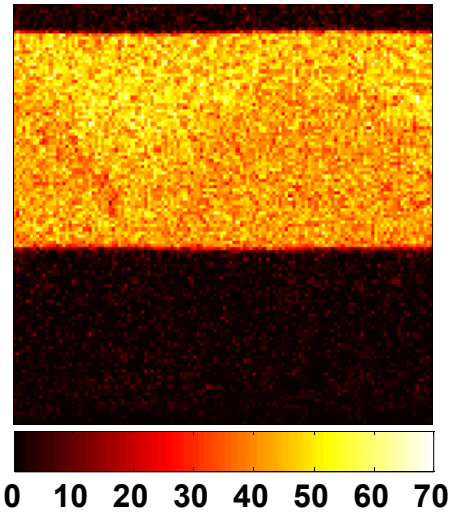
Integration and deconvolution at each pixel yields count-maps



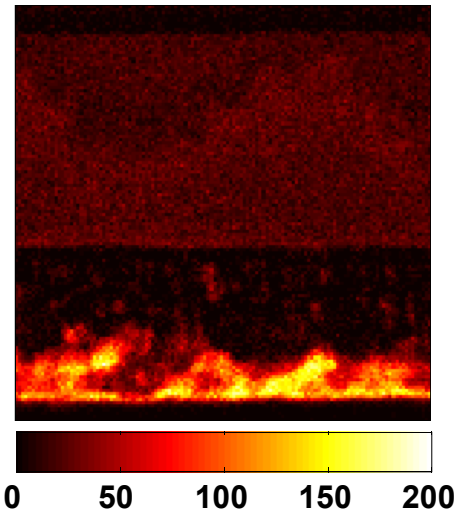
Pt counts



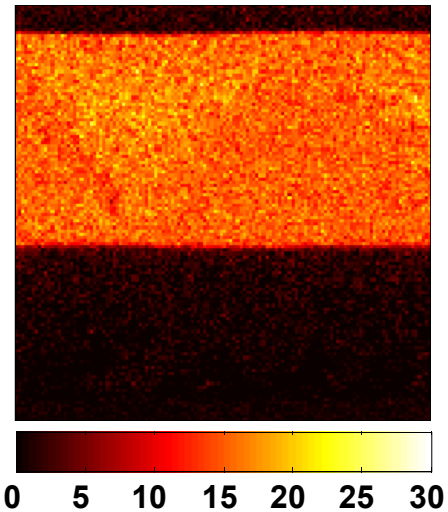
Pb counts



Zr counts



Ti counts



La counts

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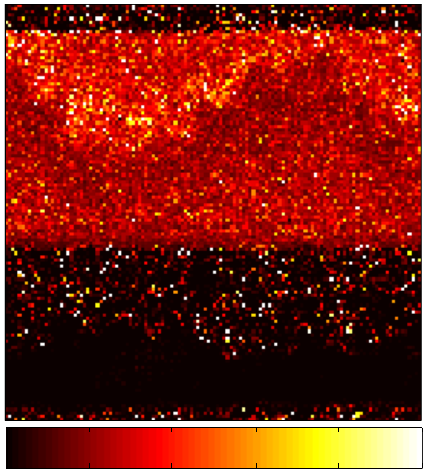
Count maps and the Cliff-Lorimer equation yield quantitative maps

Cliff-Lorimer equation:

$$\frac{C_{Zr}}{C_{Ti}} = k_{ZrTi}\frac{I_{Zr}}{I_{Ti}}$$

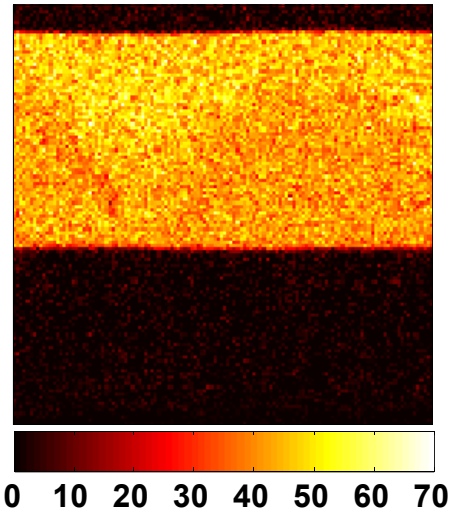
J. Micros., V103(2), 1975, P.203

Quantitative mapping:



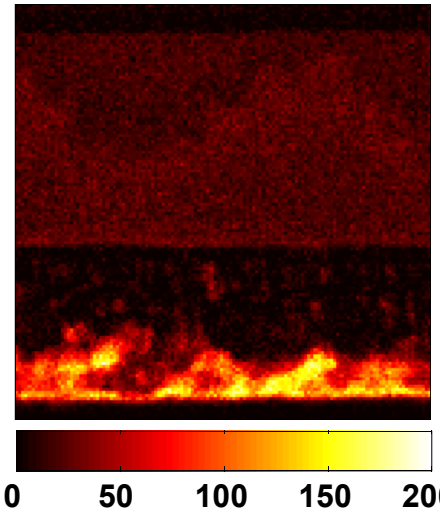
Zr/Ti cation ratio

$= k_{ZrTi} \times$



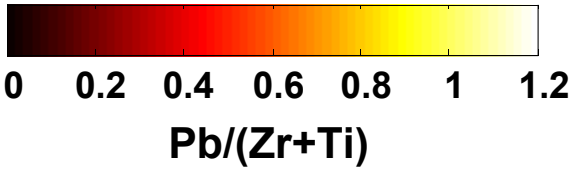
Zr counts

÷



Ti counts

The overcoat+anneal process restores the Pb-stoichiometry

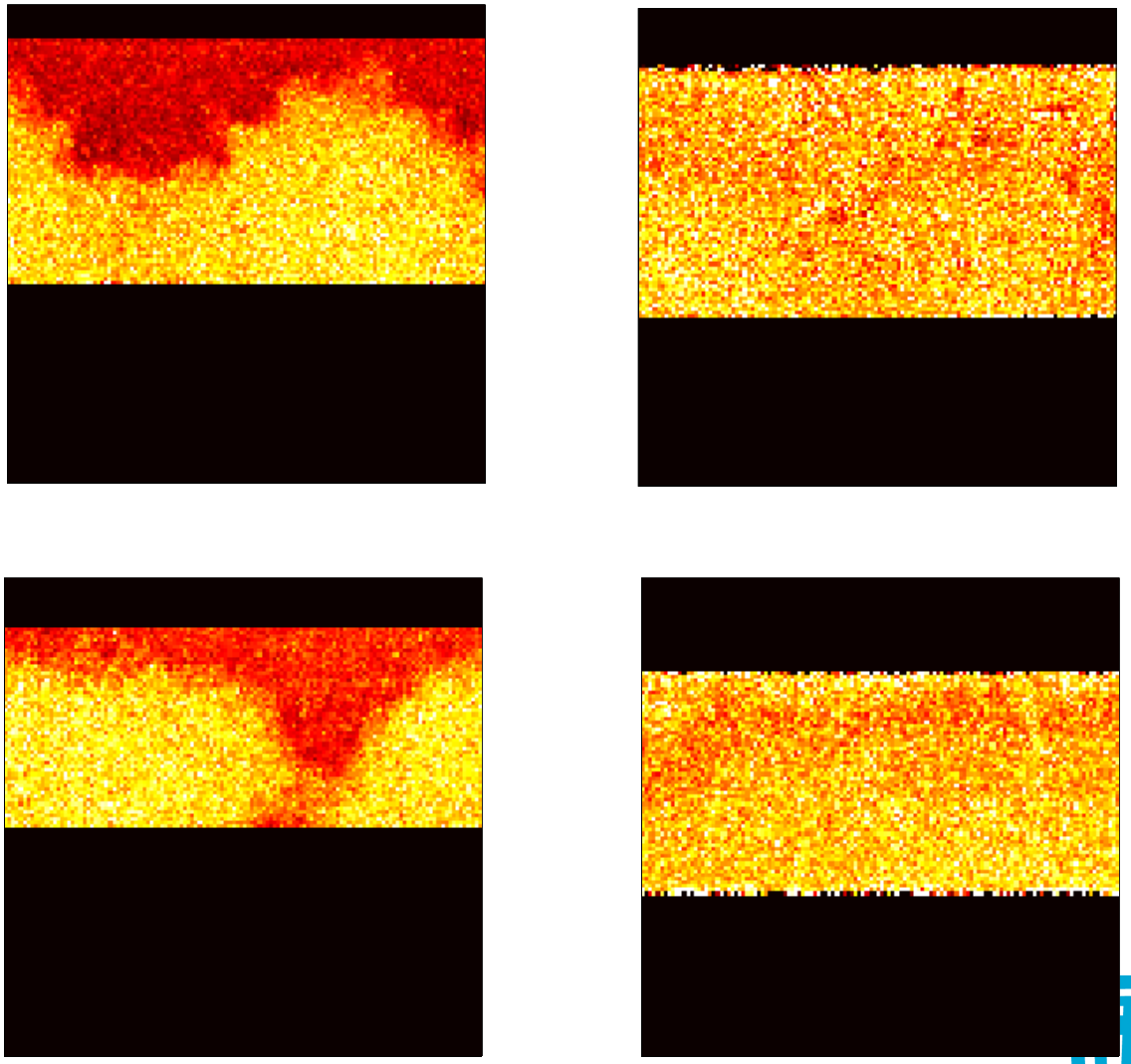


Mixed phase

Single phase

PLZT 12/70/30
650°C / 30 min

PZT 53/47
650°C / 30 min



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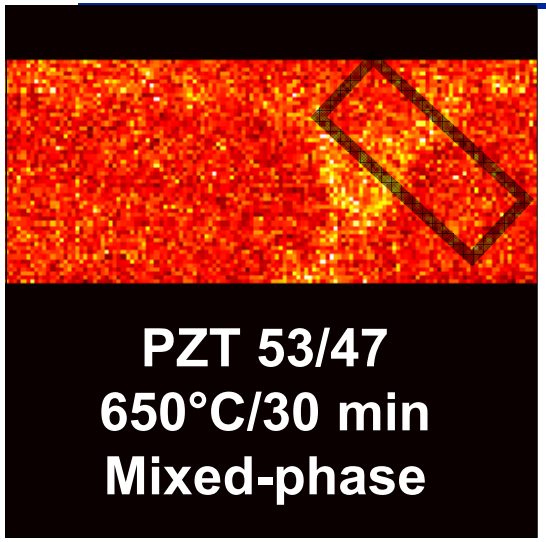
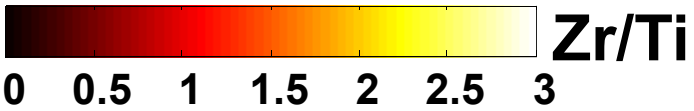
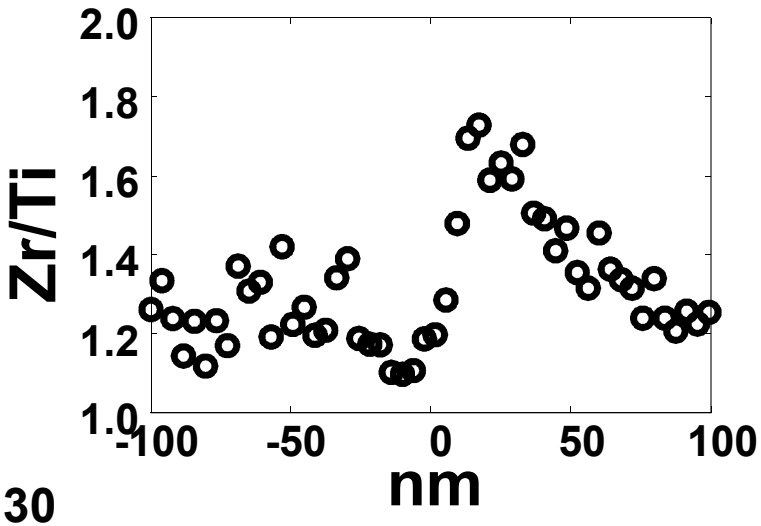
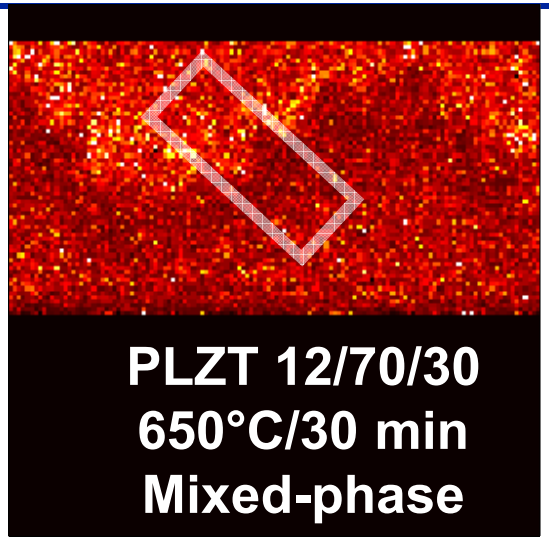
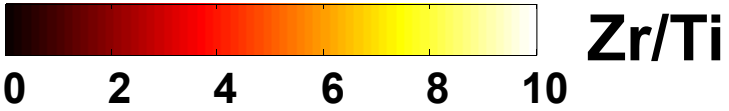
Zr segregates to the fluorite

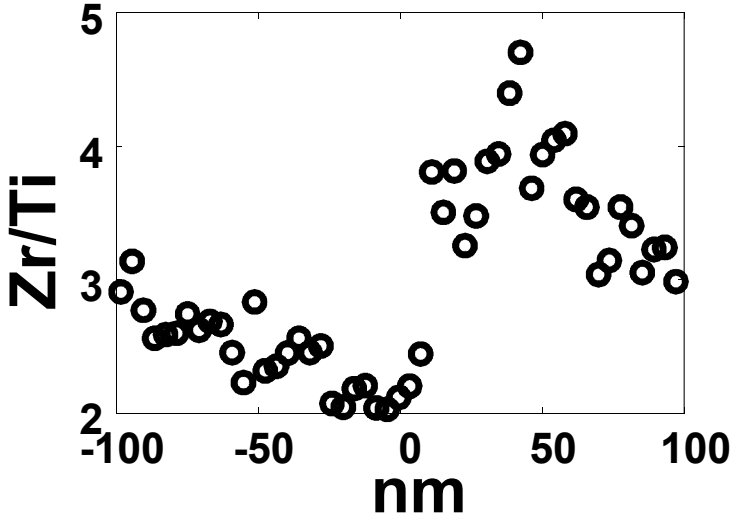




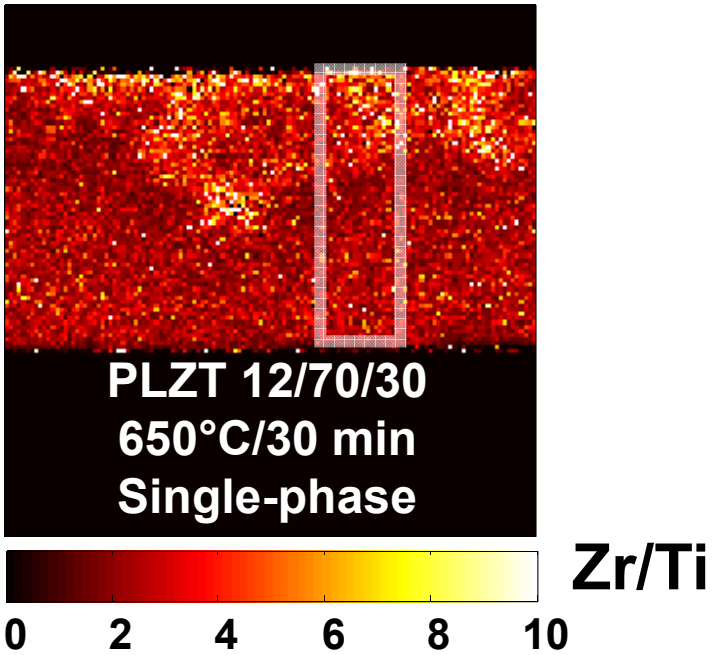


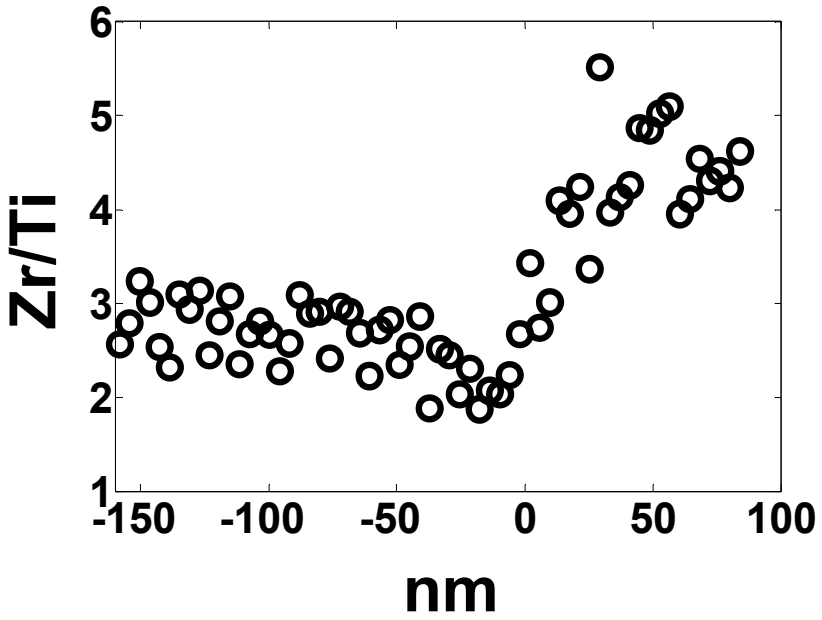






Zr segregation remains after the fluorite → perovskite conversion





However, little Zr-segregation is seen in the PZT 53/47 material

→Currently under investigation

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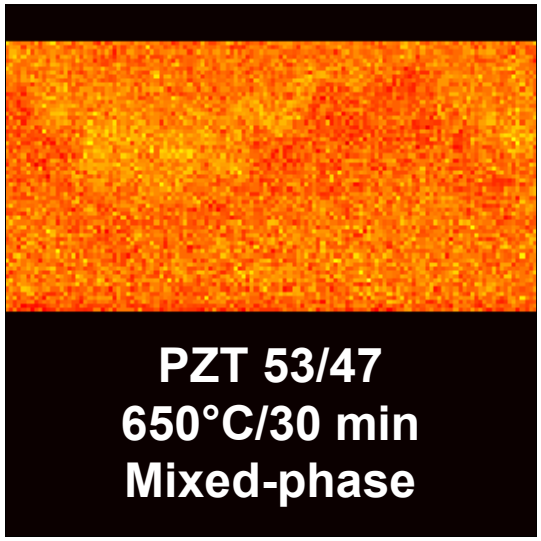
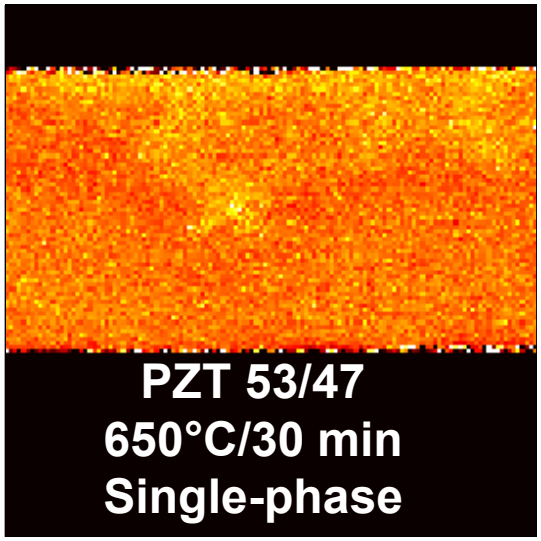
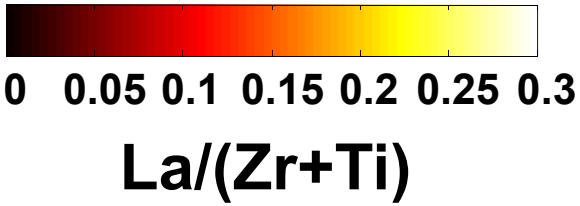
La segregation is also present







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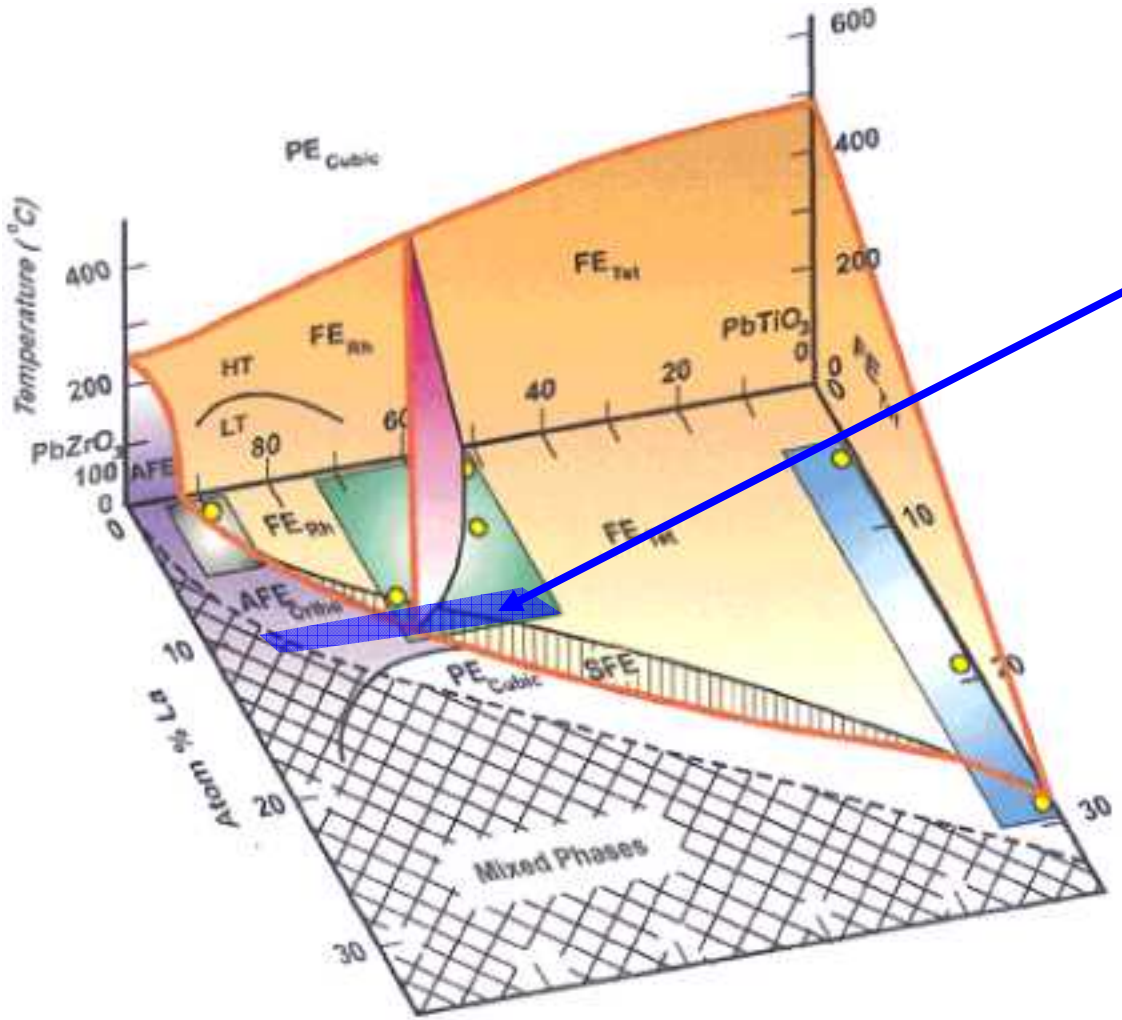
Accurate measurement of cation content is important to interpret properties



Measured chemistry crosses phase boundaries –

This may degrade properties

Haertling, J. Am. Ceram. Soc., V82, 1999, P.797

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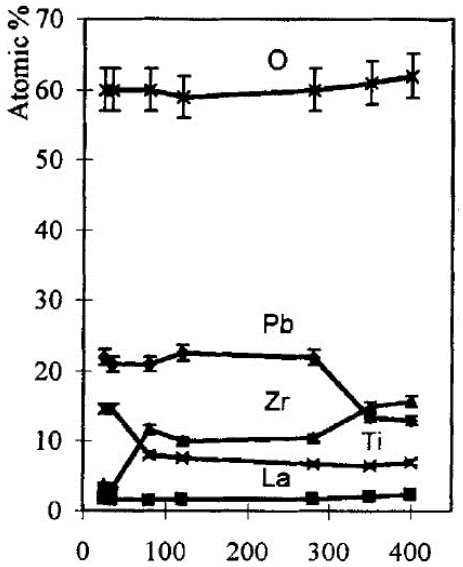
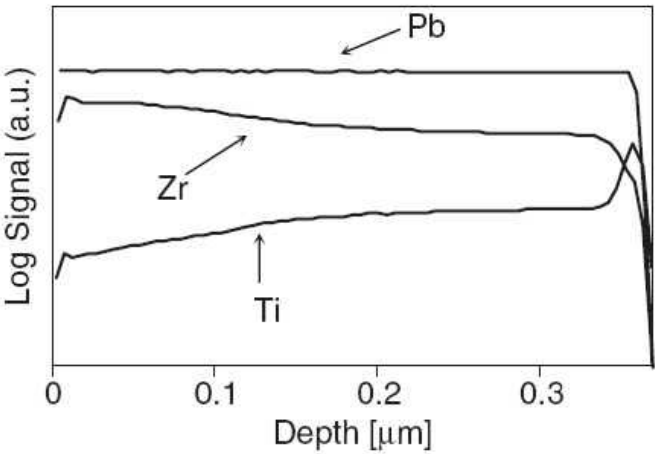
We have succeeded in mapping cations at a length scale ≈ feature size

EDS linescan:
Spot size ~10 nm



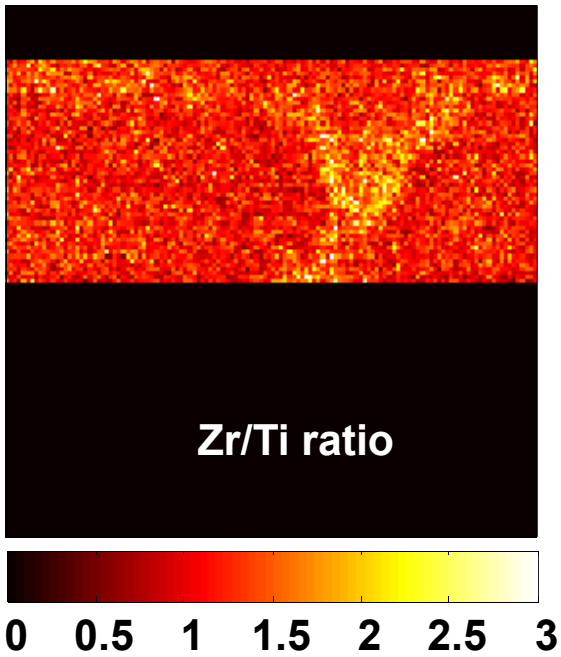
Drazic & Kosec, Ferroelectrics, V201, P.23, 1997

SIMS depth-profile:
Sampled area 40×40 μm



Etin et al., J. Am. Ceram. Soc., V89, P.2387, 2006

Quantified SI:
500×250 nm



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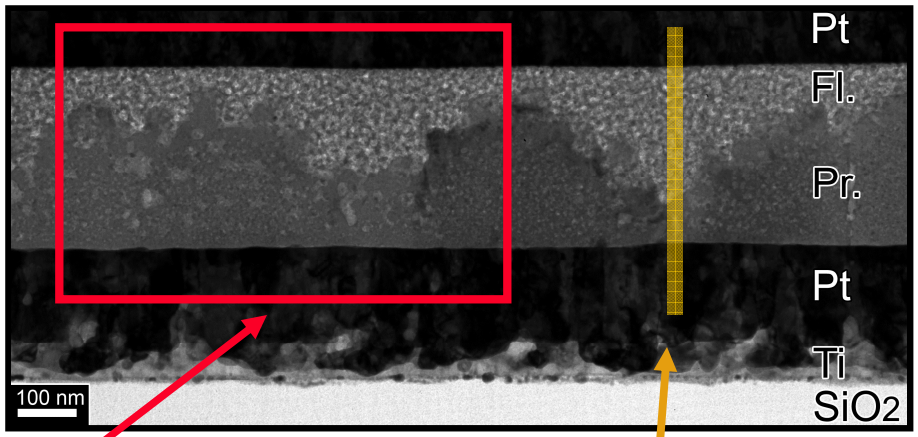
We have succeeded in mapping cations at a length scale ≈ feature size

SIMS, XPS, AES depth profiling
~several 10s of microns
≠ feature size



Feature size
~hundreds of nms

EDS linescan sampling
~several nanometers
≠ feature size

Used STEM-EDS SIs to sample this scale

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We've been able to quantify point-by-point

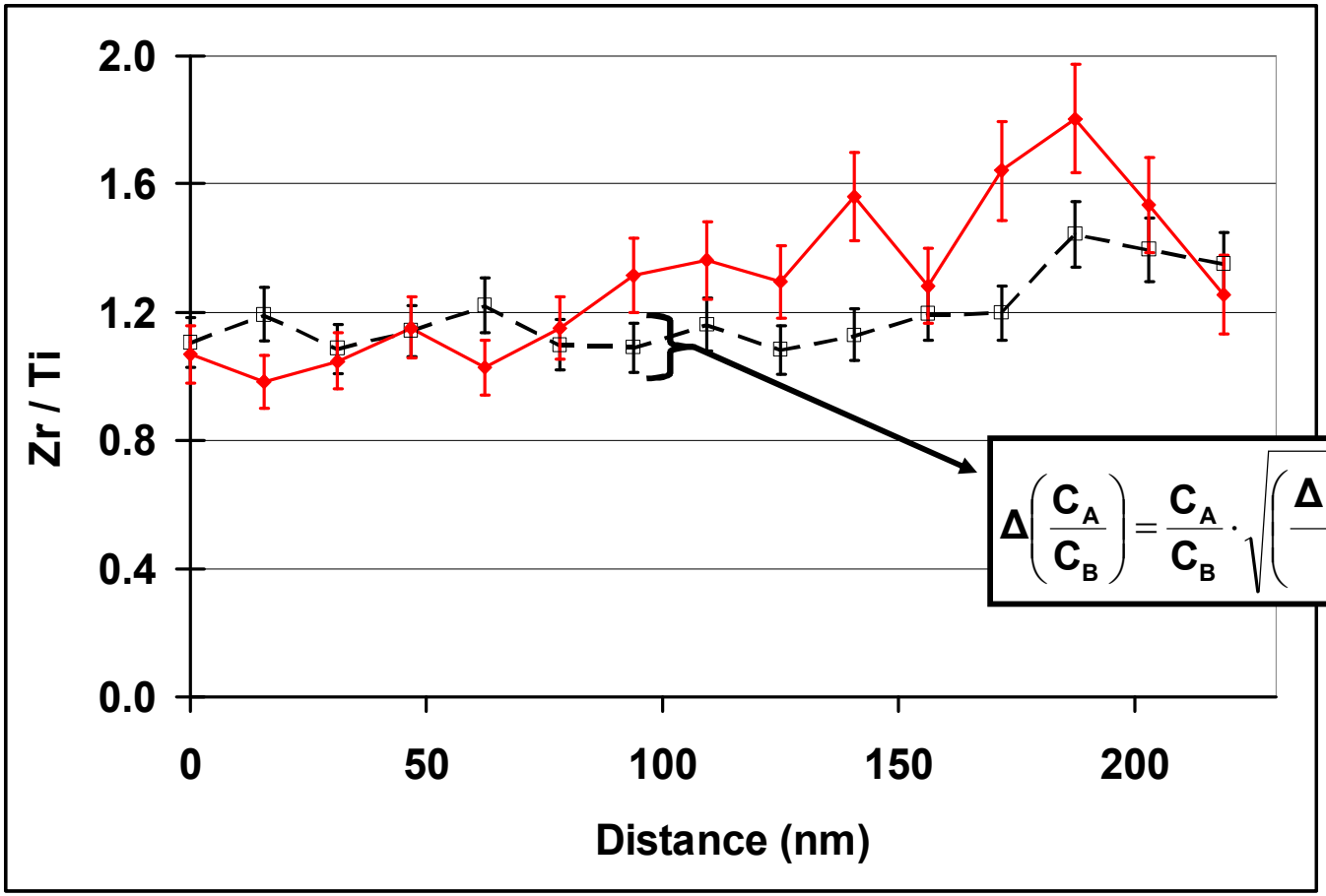
A novel overcoat+anneal technique allows us to make single-phase perovskite without excess Pb-additions

Spectrum images have the proper size scale to study inhomogeneities in PLZT thin films

Severe Zr-segregation found in PLZT but not PZT samples

PCA analysis + Cliff-Lorimer quantification allows mapping of the quantitative cation contents

What we're still missing: statistical uncertainty



In a traditional EDS point-analysis, statistical bounds are easily calculated

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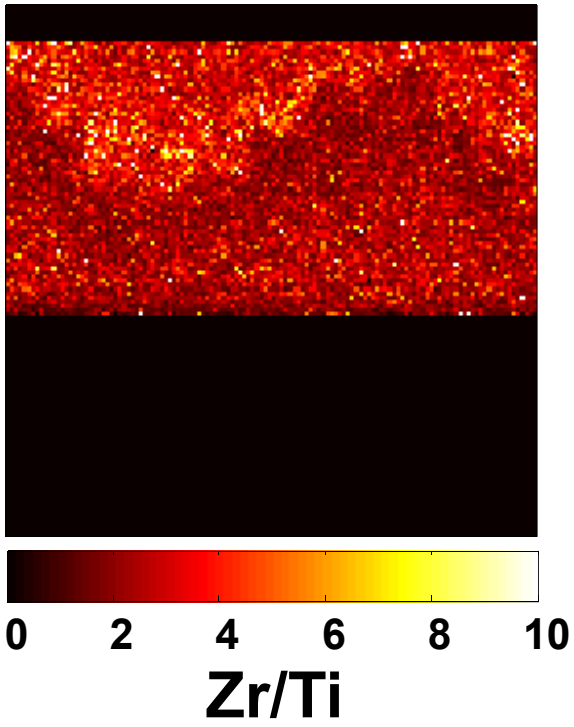
What we're still missing: statistical uncertainty



$\pm$

?

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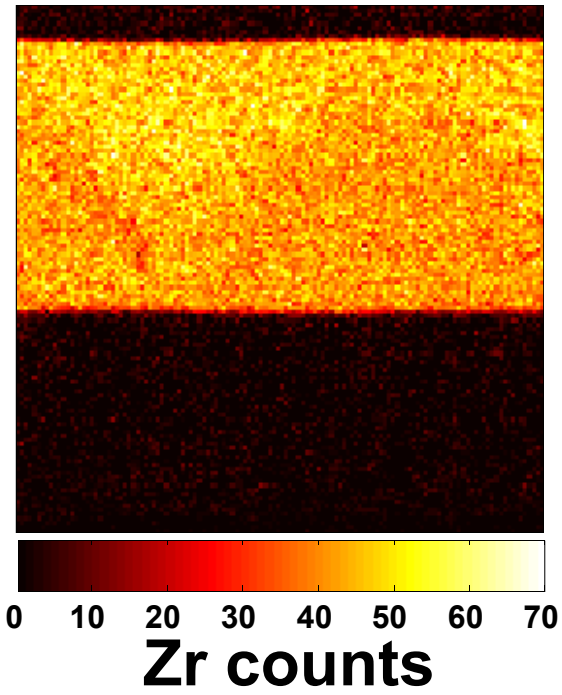
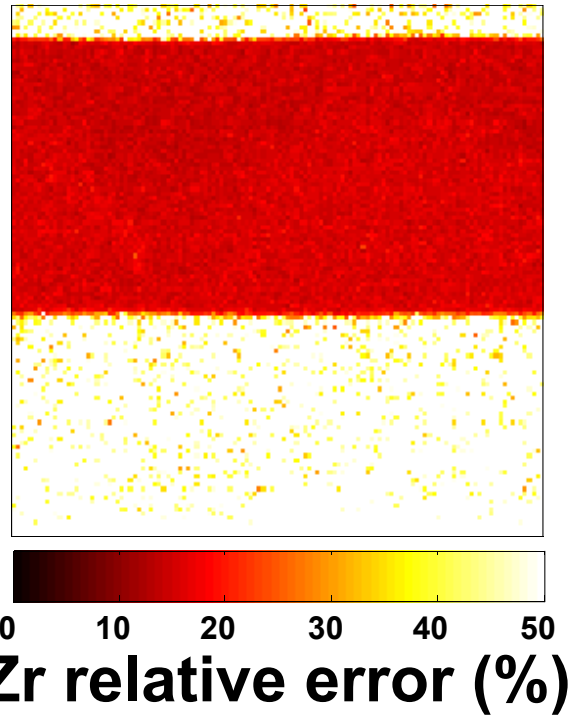
What if we apply our uncertainty equation point-by-point?

$$\Delta\left(\frac{C_A}{C_B}\right) = \frac{C_A}{C_B}\cdot\sqrt{\left(\frac{\Delta k_{AB}|_{1\sigma}}{k_{AB}}\right)^2 + \left(\frac{\sqrt{I_A}}{I_A}\right)^2 + \left(\frac{\sqrt{I_B}}{I_B}\right)^2}$$



$$\sqrt{I_{Zr}} \Big/ I_{Zr}$$



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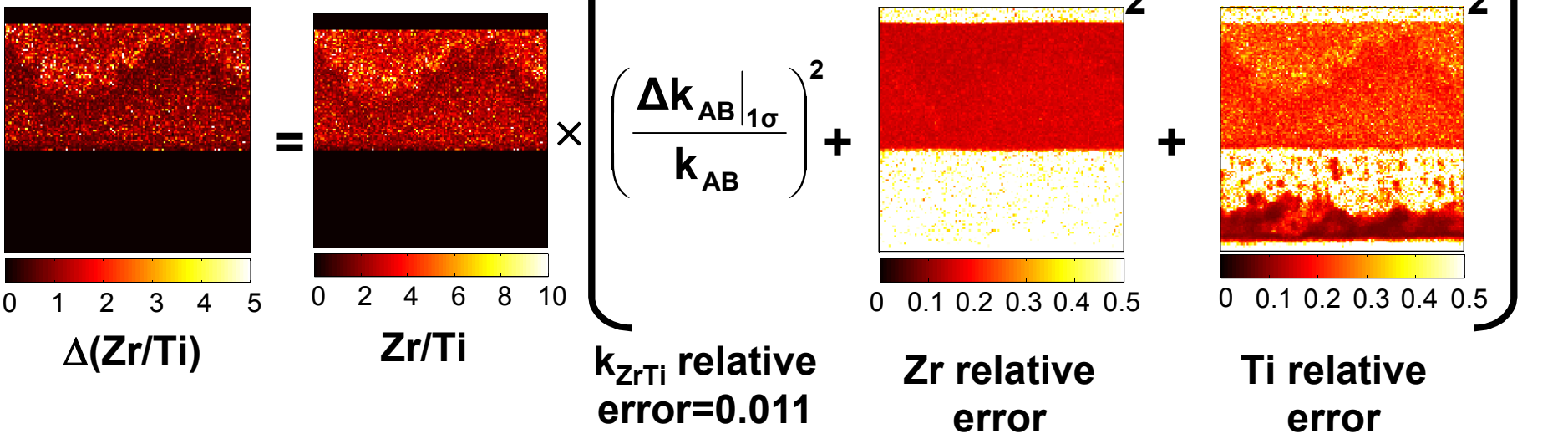
What if we apply our uncertainty equation point-by-point?

$$\Delta\left(\frac{C_A}{C_B}\right) = \frac{C_A}{C_B}\cdot\sqrt{\left(\frac{\Delta k_{AB}|_{1\sigma}}{k_{AB}}\right)^2 + \left(\frac{\sqrt{I_A}}{I_A}\right)^2 + \left(\frac{\sqrt{I_B}}{I_B}\right)^2}$$



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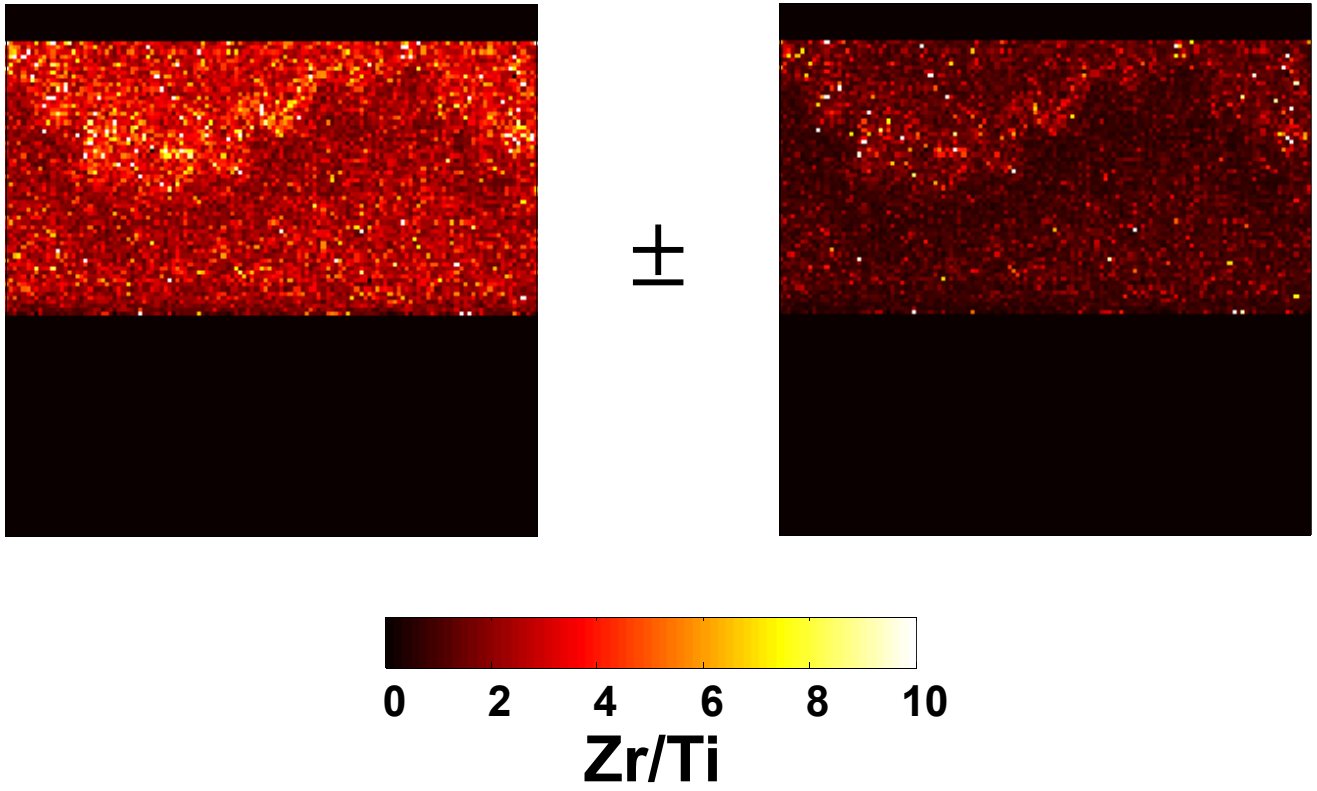
We thus have cation fraction and uncertainty with <≈ 10 nm resolution



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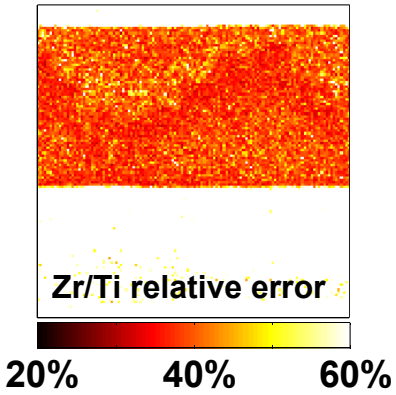
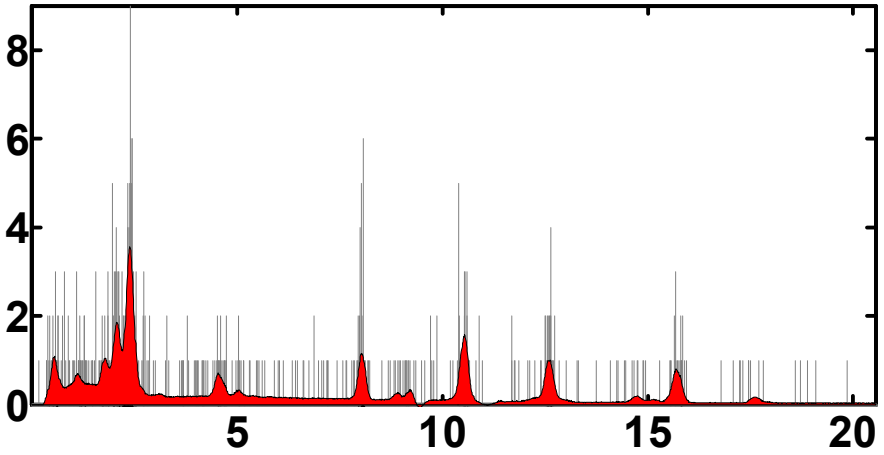
These uncertainties are very large – how to do better?

Uncertainties are ≈20-40% relative:



This is a result of the small # counts/pixel:



How can we use MSA to improve our statistics?

PCA solutions can be mathematically rotated

PCA solution:

$$\mathbf{D} \approx \mathbf{C}\mathbf{S}^{\mathsf{T}}$$

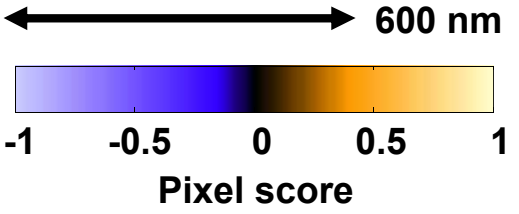
D=*data*
C=*score images*
S=*loading spectra*

For some rotation *R*:

$$\mathbf{D} \approx \tilde{\mathbf{C}}\tilde{\mathbf{S}}^{\mathsf{T}} = \left(\mathbf{C}\mathbf{R}\right)\left(\mathbf{R}^{-1}\mathbf{S}^{\mathsf{T}}\right)$$

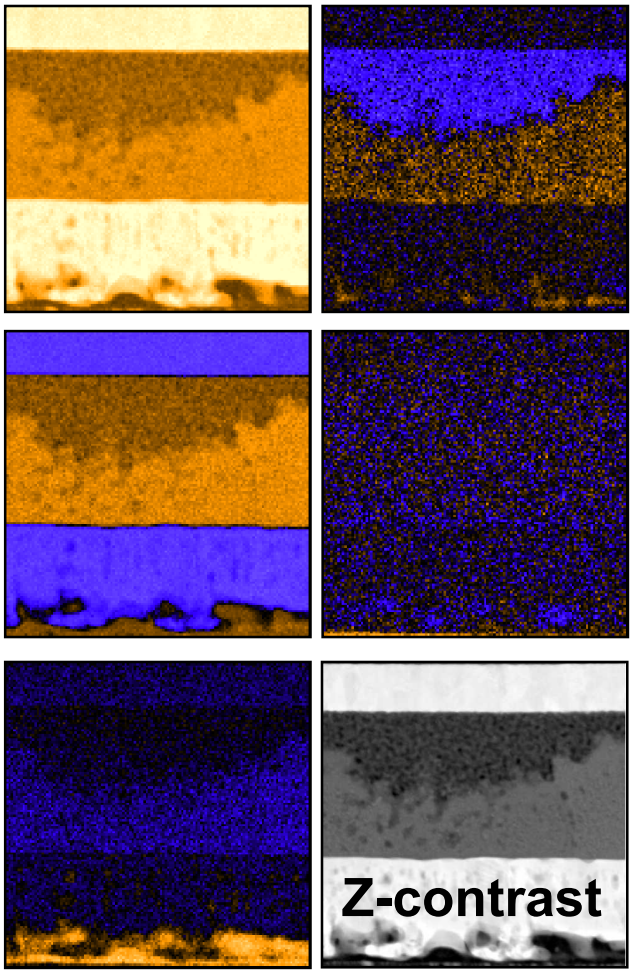
Choose *R* to maximize spatial contrast

Rotate into a spatially-simple case



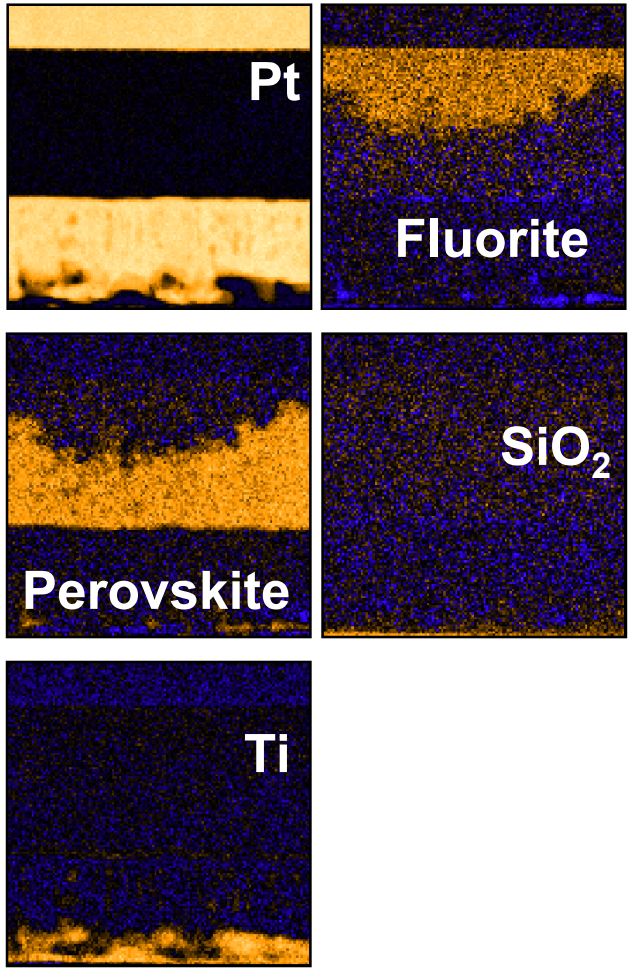
Highly mixed score images

High-contrast score images

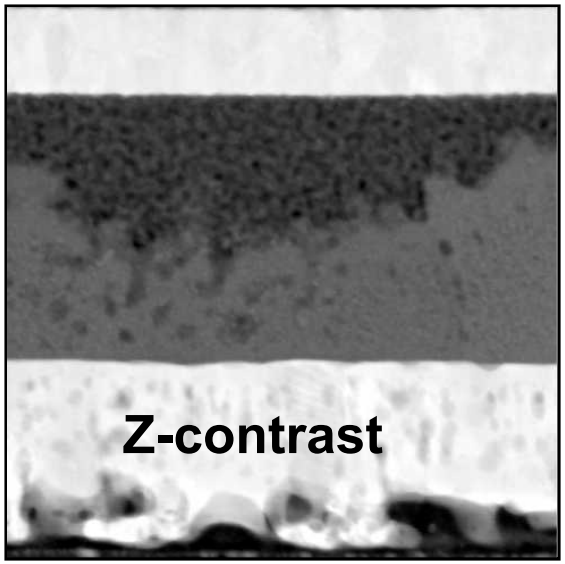


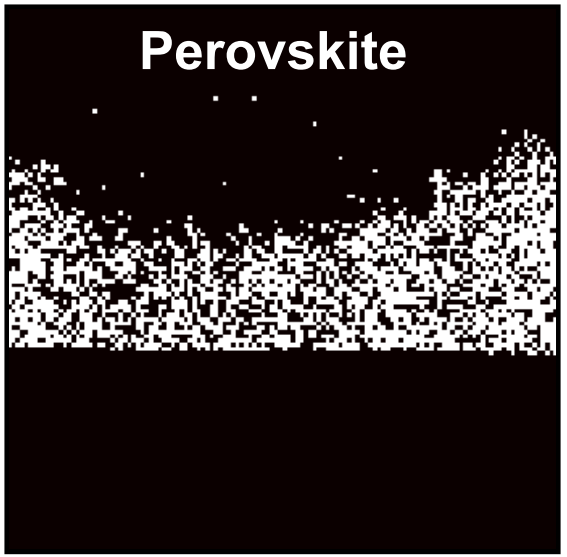
$C \rightarrow \tilde{C}$

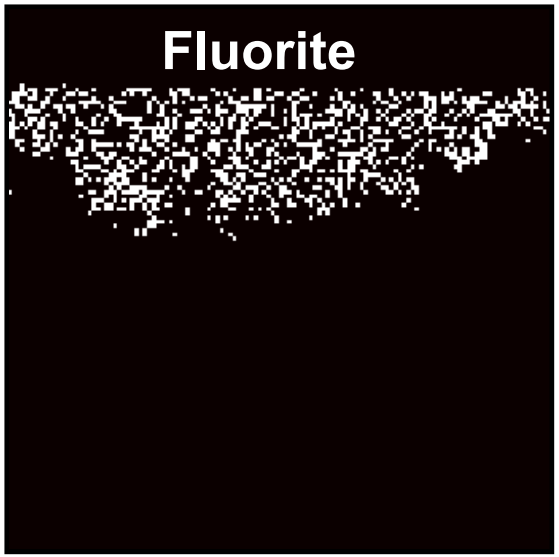
$S \rightarrow \tilde{S}$

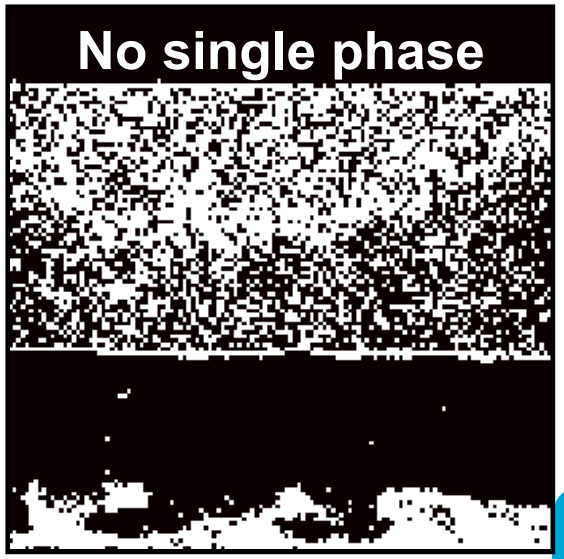


If ≥70% of the counts in a pixel are from one PC, define it as single-phase









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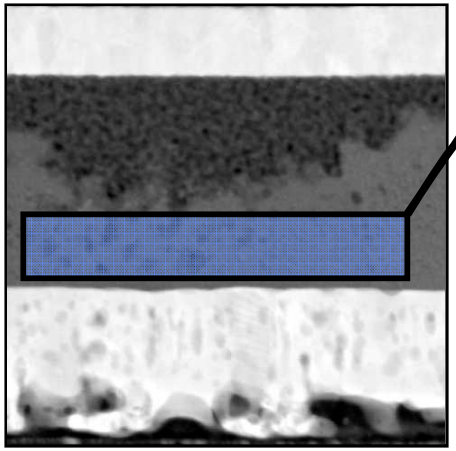
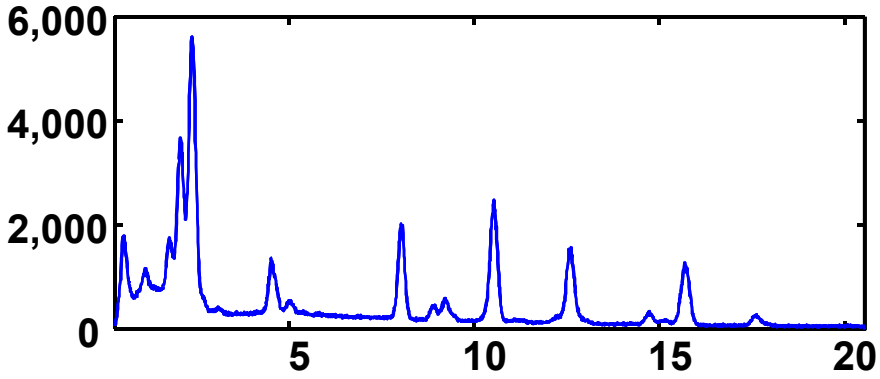
This is an unbiased way to perform phase analyses

Manual method:

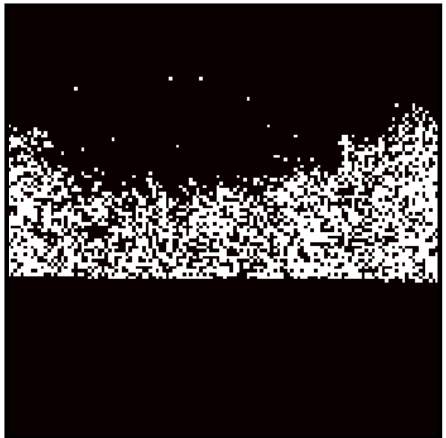
Choose a box with STEM software

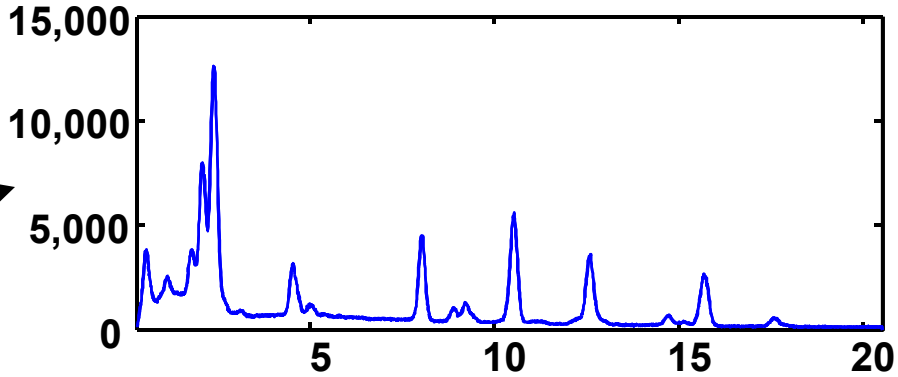




This method:

After-the-fact statistical selection





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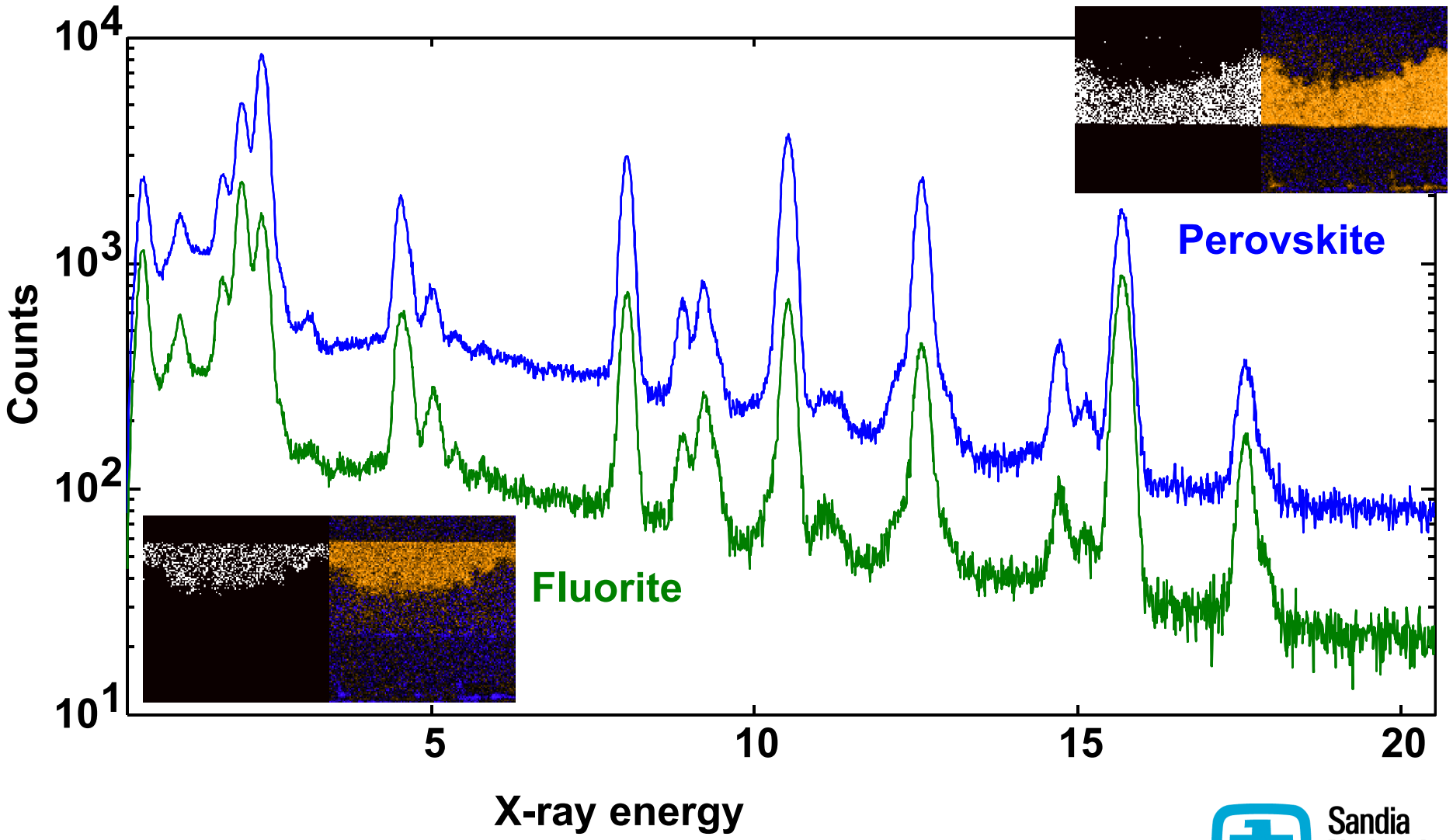
This is an unbiased way to perform phase analyses



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It's possible to use MSA to define phase boundaries for quantification

Single-pixel analysis gave 5-10 nm resolution, but ≈30% errors (±1σ) in cation content

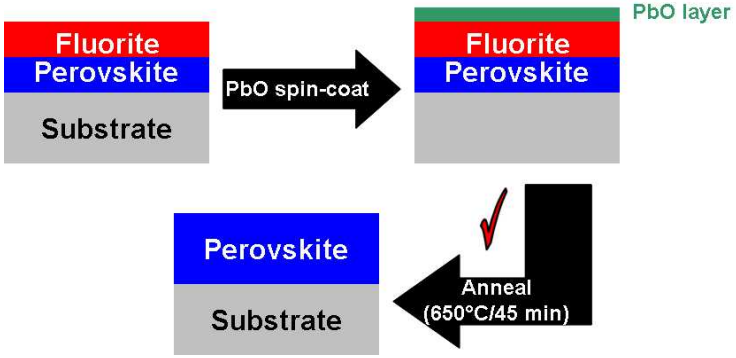
With MSA-defined phases, <10% error (±3σ) in quantification:

	Cation fraction ratio				Cation fraction			
	Pb/(Zr+Ti)	Zr/Ti	La/Pb	La/(Zr+Ti)	Pb	Zr	Ti	La
Perovskite	0.86 ± 0.03	2.09 ± 0.14	0.18 ± 0.03	0.16 ± 0.02	43%	34%	16%	8%
Fluorite	0.34 ± 0.02	3.85 ± 0.28	0.52 ± 0.07	0.18 ± 0.02	22%	53%	14%	12%

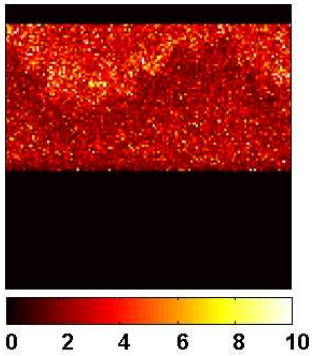
Of course, we can't speak about variations within a phase – we're assuming it's homogenous

We've quantified PLZT chemistry at high resolution, and are studying the statistics

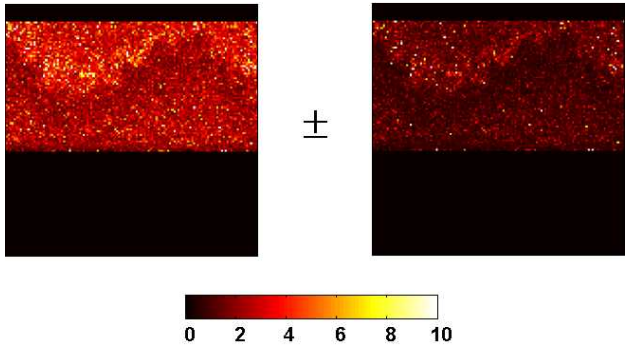
We produced single-phase perovskite without excess Pb-additions



Quantification of spectrum images allowed high-resolution study of segregation



We're exploring statistical error in quantitative SIs

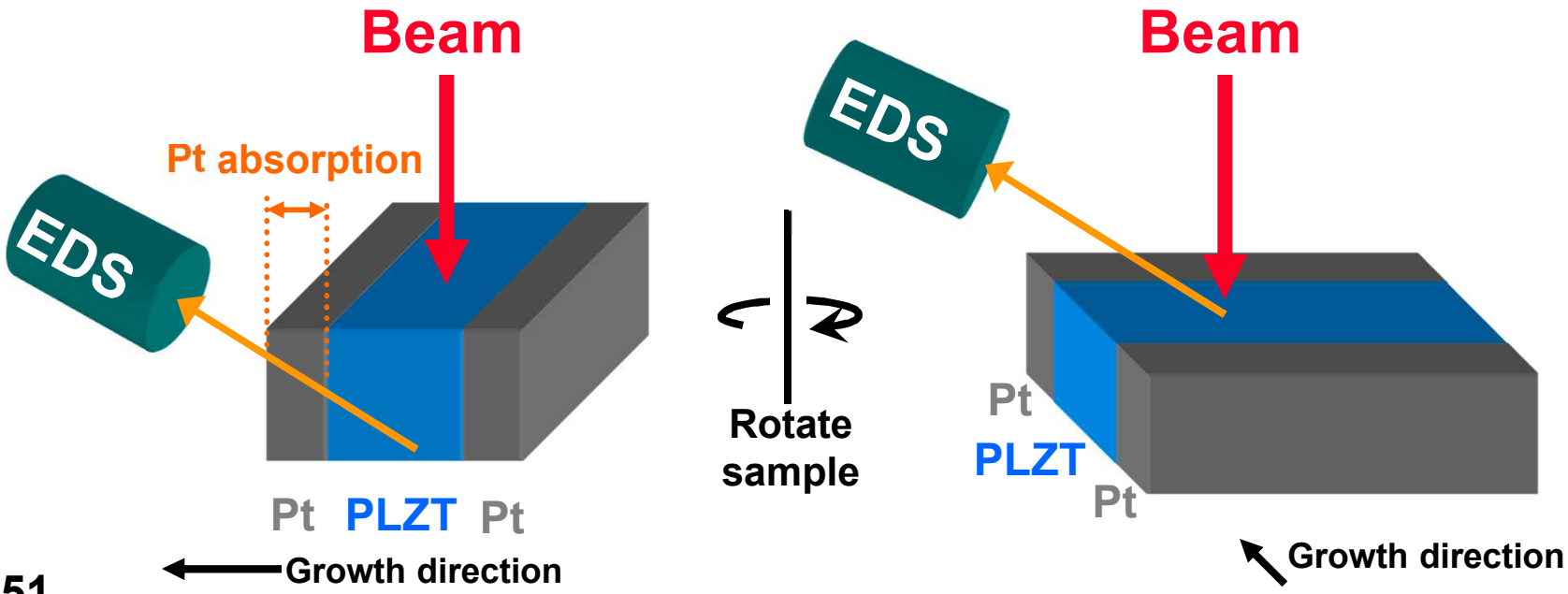


Platinum electrodes must be accommodated for

Platinum electrodes are sputtered above and below the films

Platinum will strongly absorb X-rays of interest

Should use a tilt-rotation holder in TEM to point the interfaces directly at the EDS to avoid absorption

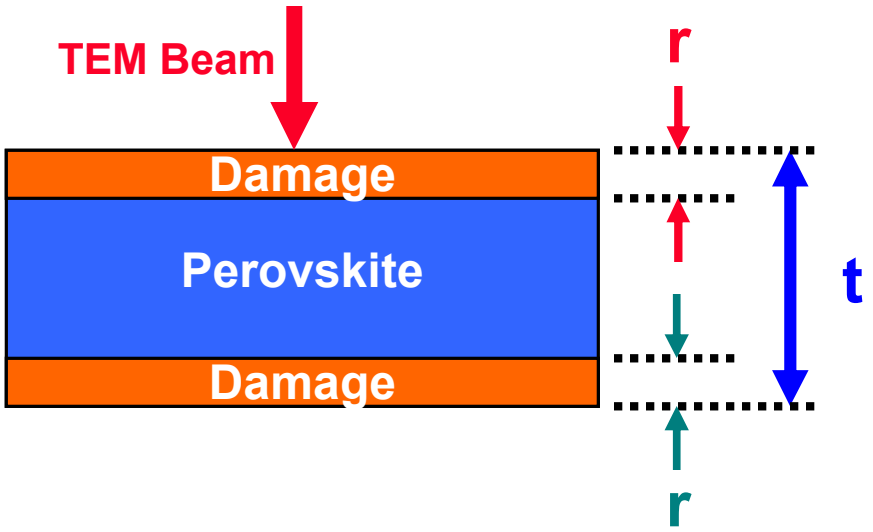


Errors in Pb quantification?

Oddly, the perovskite PZT is measured ~20% Pb deficient

→ **Real or artifact? Still under investigation**

Theory: Damage from FIB sample preparation



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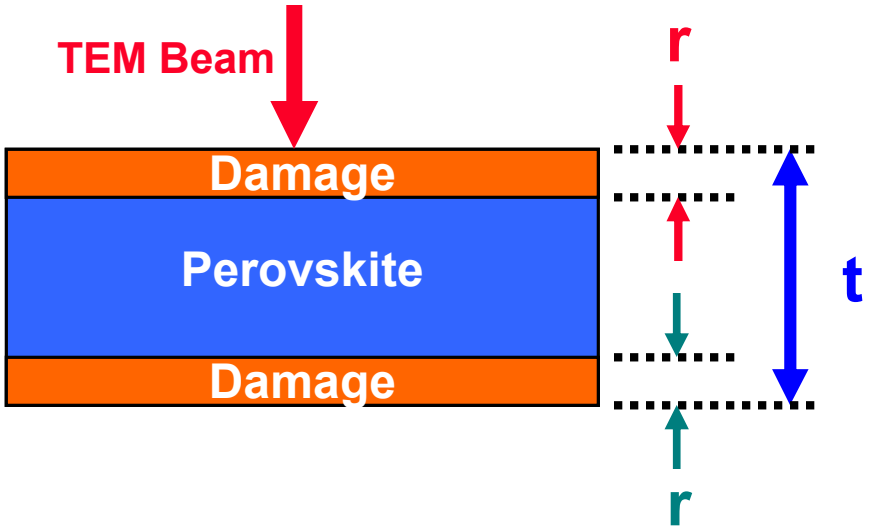
Errors in Pb quantification?



Let's make some assumptions:

t **=100 nm**

Perovskite is (*t*-2*r*) thick, and has C_{Pb}=0.5

Damaged layers are each *r* thick, and have C_{Pb}=0.25

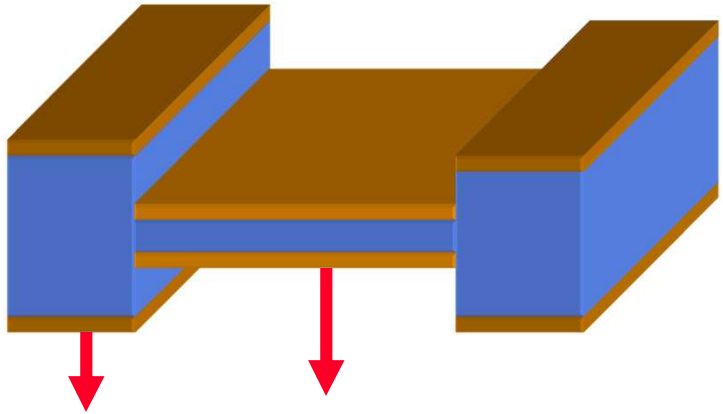
EDS measured C_{Pb} = (0.5 × (t-2r)) + (0.25 × 2r)=0.4

Thus, r≈20nm ← *reasonable for FIB-damage*

Errors in Pb quantification?

Further analysis:

- FIB-lift out sections are dog-bone shaped
- EDS of different thicknesses → different Pb-fractions



Measured C_{Pb}: ~0.48 ~0.40

- Assume the thick section has t=300 nm, r=20 nm
- Assume C_{Pb} of 0.50 and 0.25 in thick-section perovskite and damaged layer

Expect to measure C_{Pb}~0.46; actually measure C_{Pb}~0.48

Spatial resolution

$$b = 7.2\times10^{5}\left(\frac{\langle Z\rangle}{E_0}\right)\left(\frac{\rho}{\langle A\rangle}\right)^{\frac{1}{2}}(t)^{\frac{3}{2}}$$

$$R = \frac{\left[d + \left(b^2 + d^2\right)^{\frac{1}{2}}\right]}{2\sqrt{2}}$$

<Z> = average atomic number
<A> = average atomic mass [=] g/mol
E_0 = beam energy [=] eV
ρ = density [=] g/cm^3
d = spot size [=] cm
t = thickness [=] cm

Michael et al. J. Micros., V160, P.41 (1990)
Reed, Ultramic., V7, P.405 (1982)

Pixel size 3.9 nm