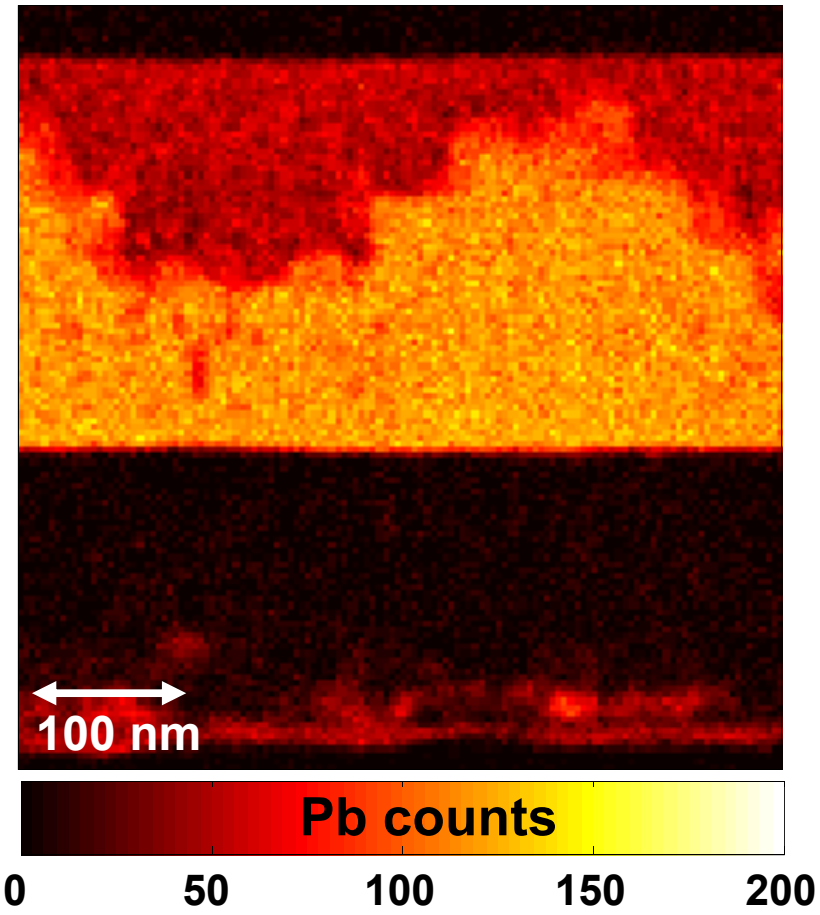
SAND2008-4795P

Quantitative STEM-EDS Spectrum Imaging of Phase Transformations in $(Pb,La)(Zr,Ti)O_3$



Chad Parish

Geoff Brennecka

Bruce Tuttle

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Materials Science and Engineering

Acknowledgements:

Michael Rye, Garry Bryant, Paul Kotula, Joe Michael, Mike Keenan

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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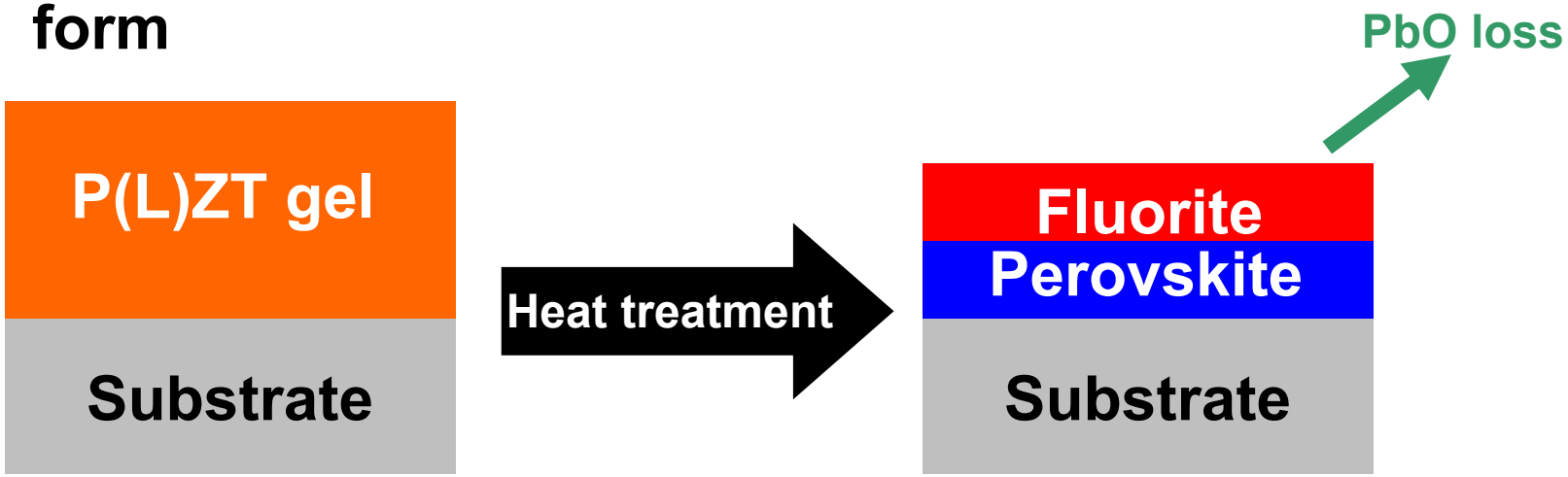
PZT & PLZT used in thin-film capacitors

$Pb(Zr,Ti)O_3$ and $(Pb,La)(Zr,Ti)O_3$ have high dielectric constant in the perovskite phase

Pb-loss during processing causes fluorite phase to form

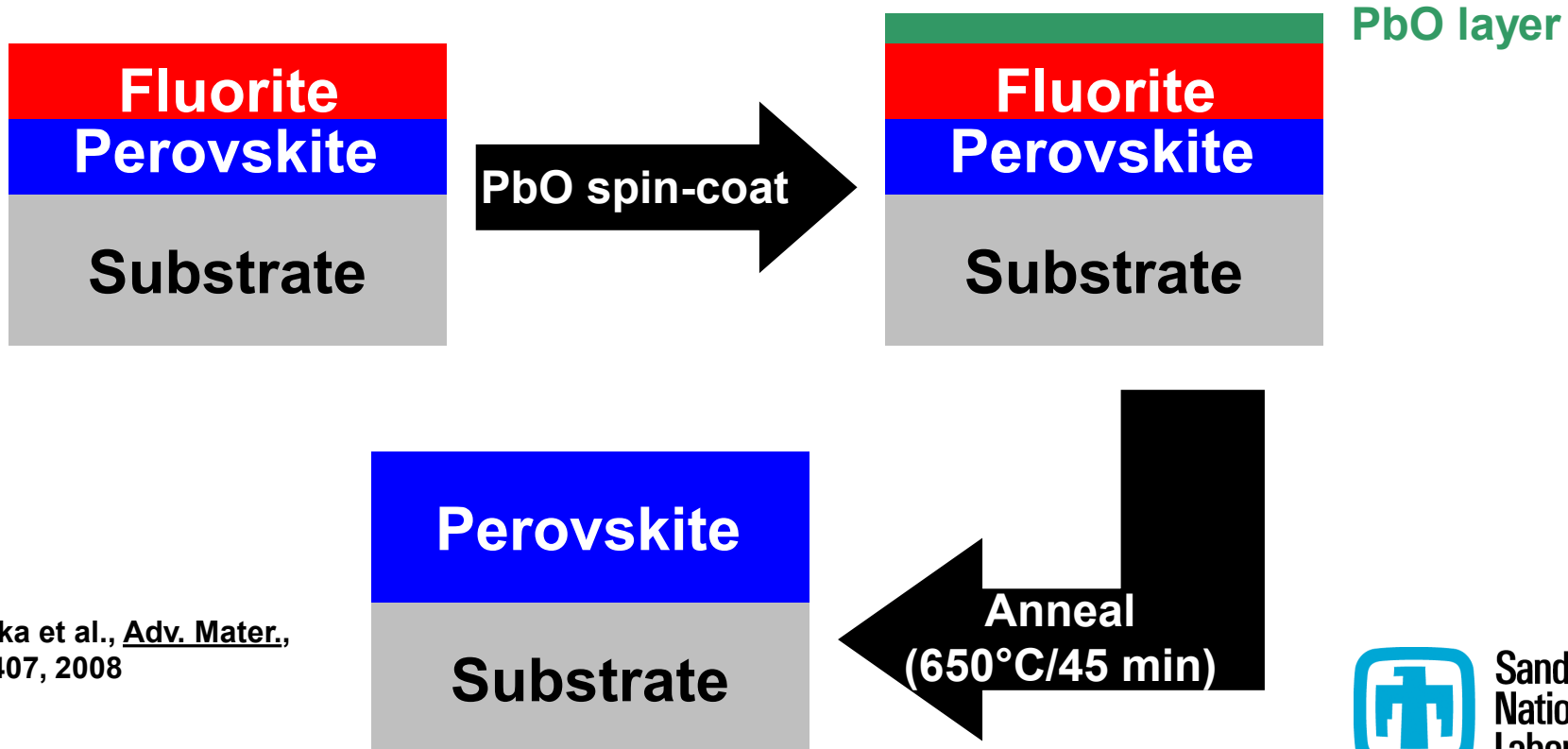


Act as series capacitors → degraded properties

XRD, HREM, and electrical properties confirm the hypothesis

We coated mixed-phase samples with PbO

PbO-overcoat + anneal yields fluorite → perovskite transformation



Brennecka et al., Adv. Mater., V20, P.1407, 2008

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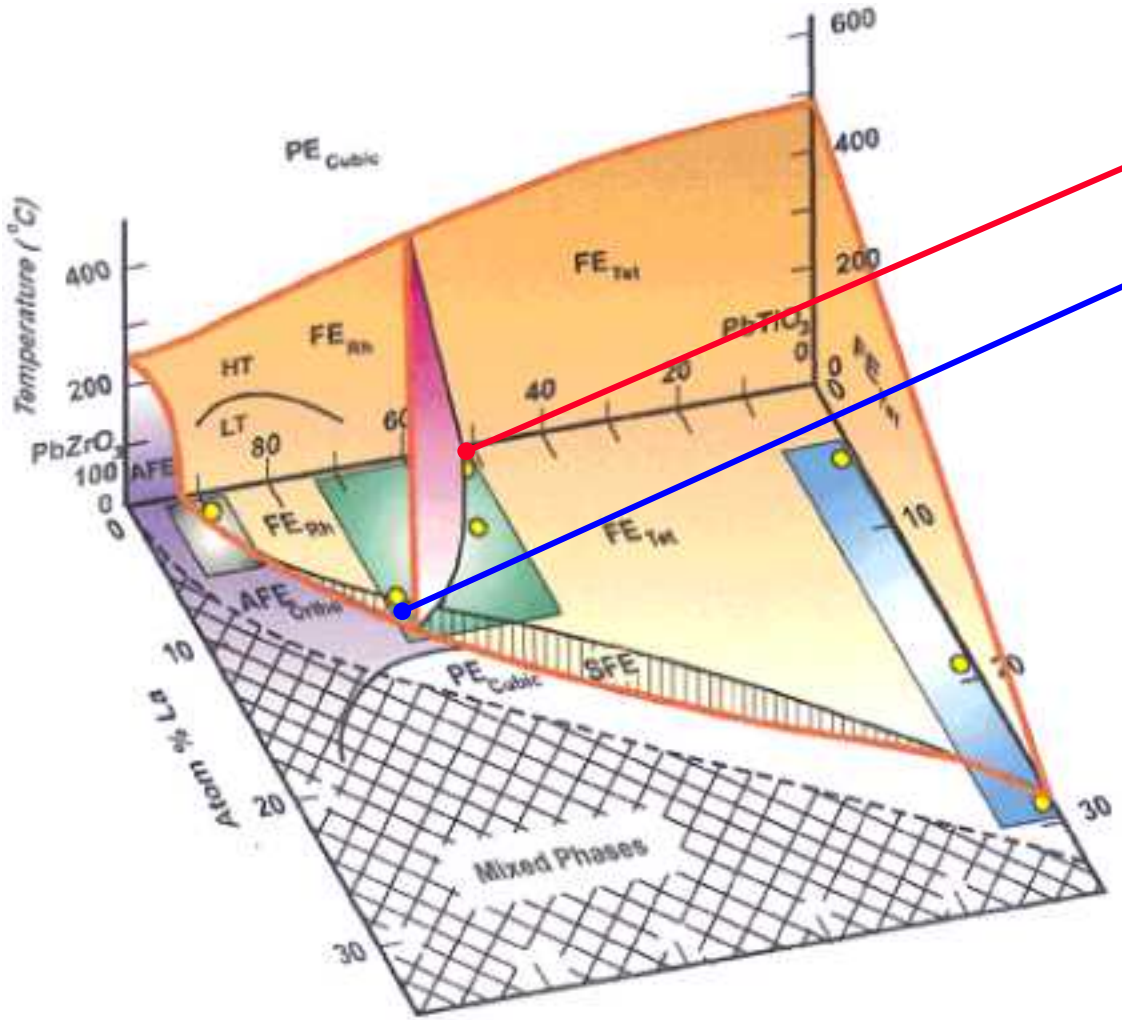
Accurate measurement of cation content is important to interpret properties



PZT 53/47

PLZT 12/70/30

In general, dielectric properties best at phase boundaries

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

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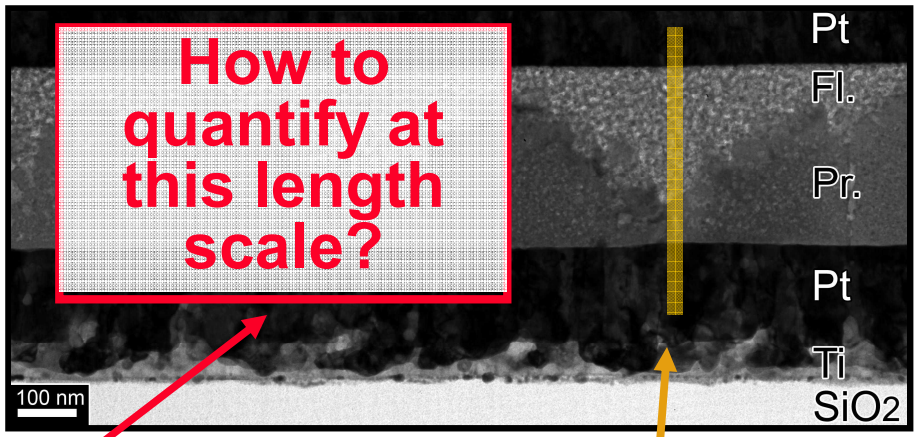
We need a technique to measure representative cation ratios

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



200 nm

Feature size
~hundreds of nms

EDS linescan sampling
<10 nm
≠ feature size

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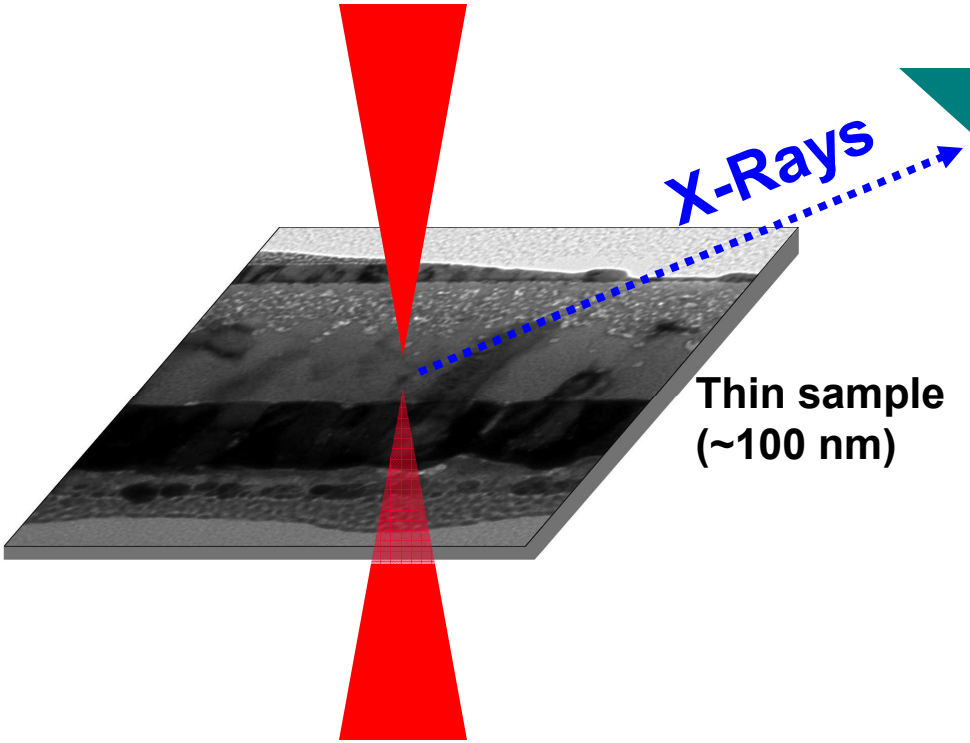
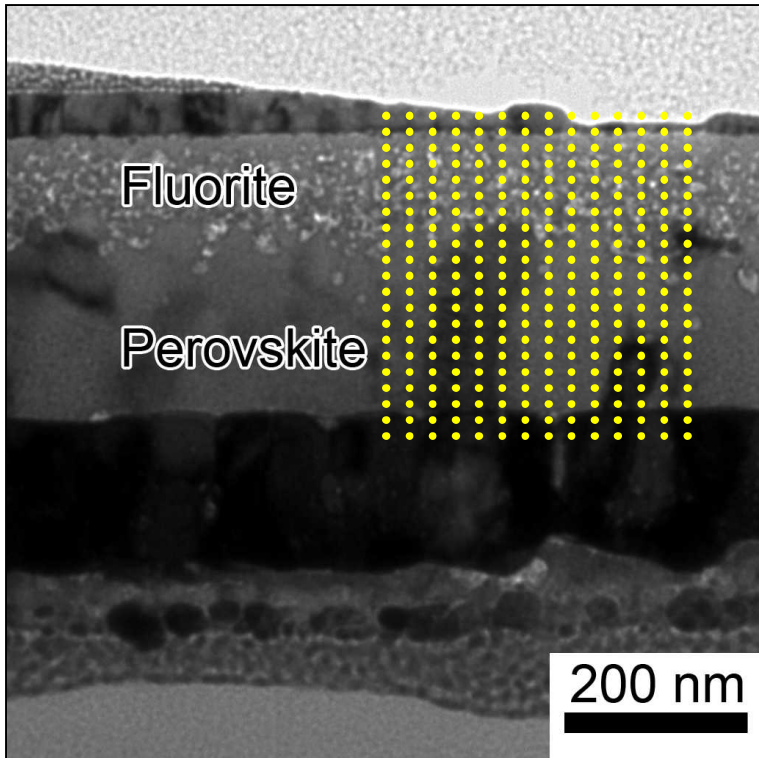
X-ray spectrum imaging in STEM used to measure local cation content

Scanning TEM (STEM) beam

EDS: Energy-dispersive X-ray spectroscopy

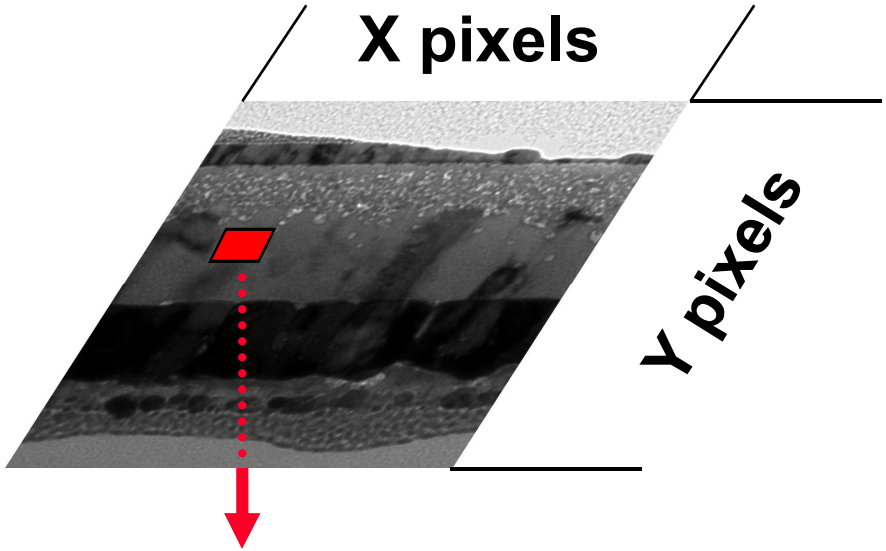
EDS detector

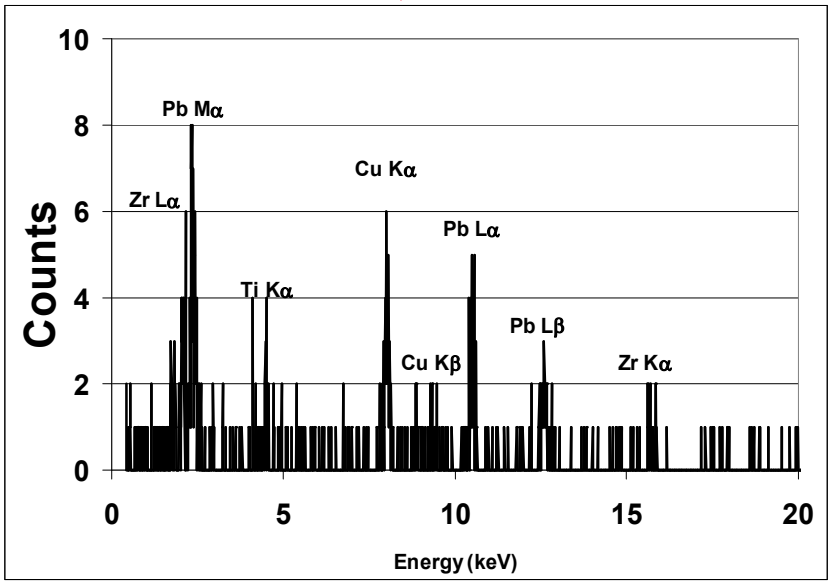




Spectrum image:
Acquire a full spectrum at many (x,y) points

Spectrum imaging – need to mine the data





Typical dataset:

128×128 pixels

2048 channels/pixel

∴ 34 million datapoints

200 msec/pixel → noisy data

How to make use of this?

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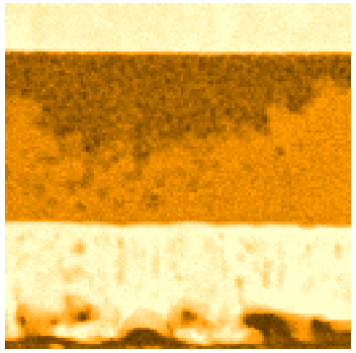
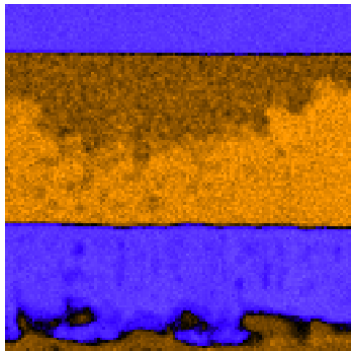
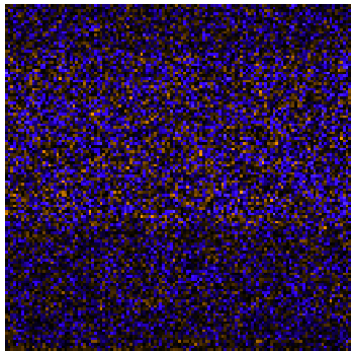
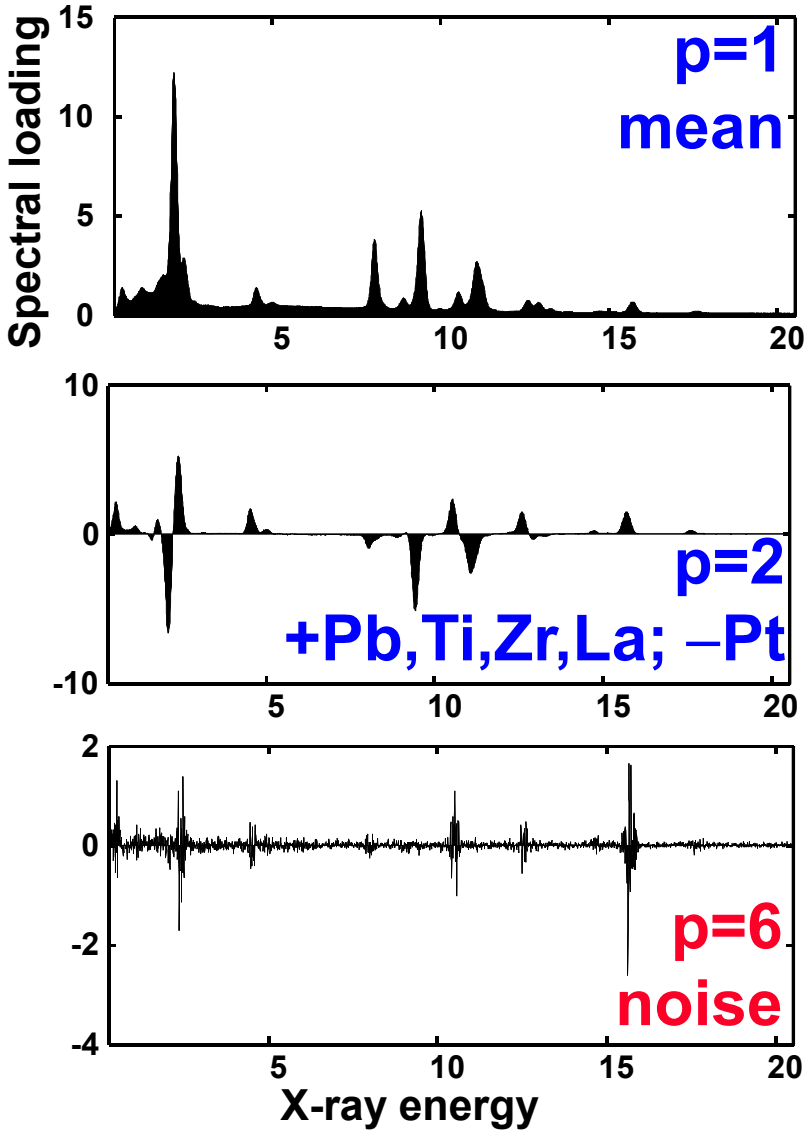
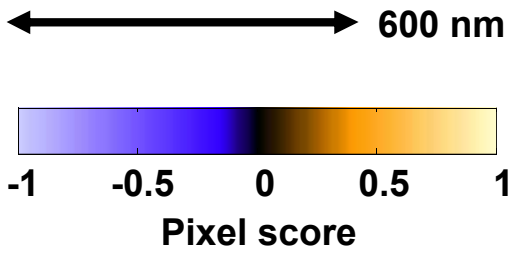
Principal component analysis (PCA): finds chemically relevant variation, rejects noise

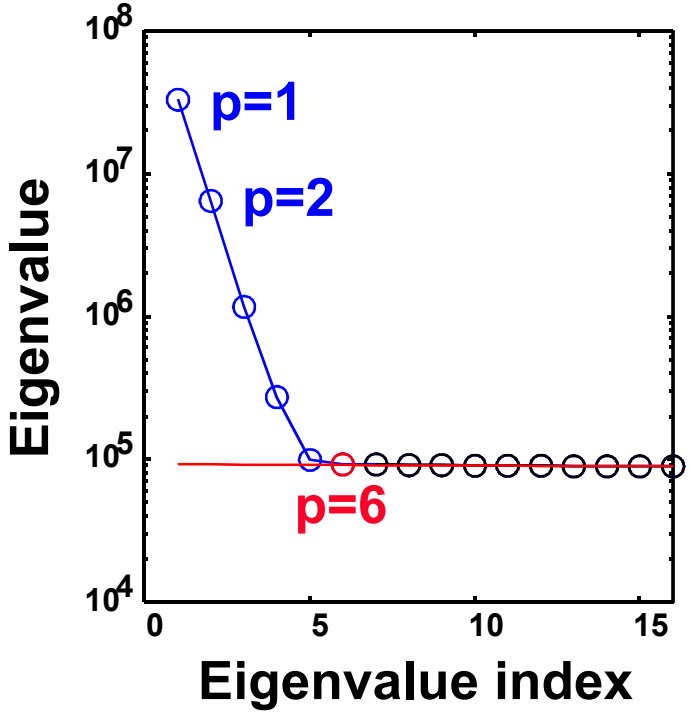












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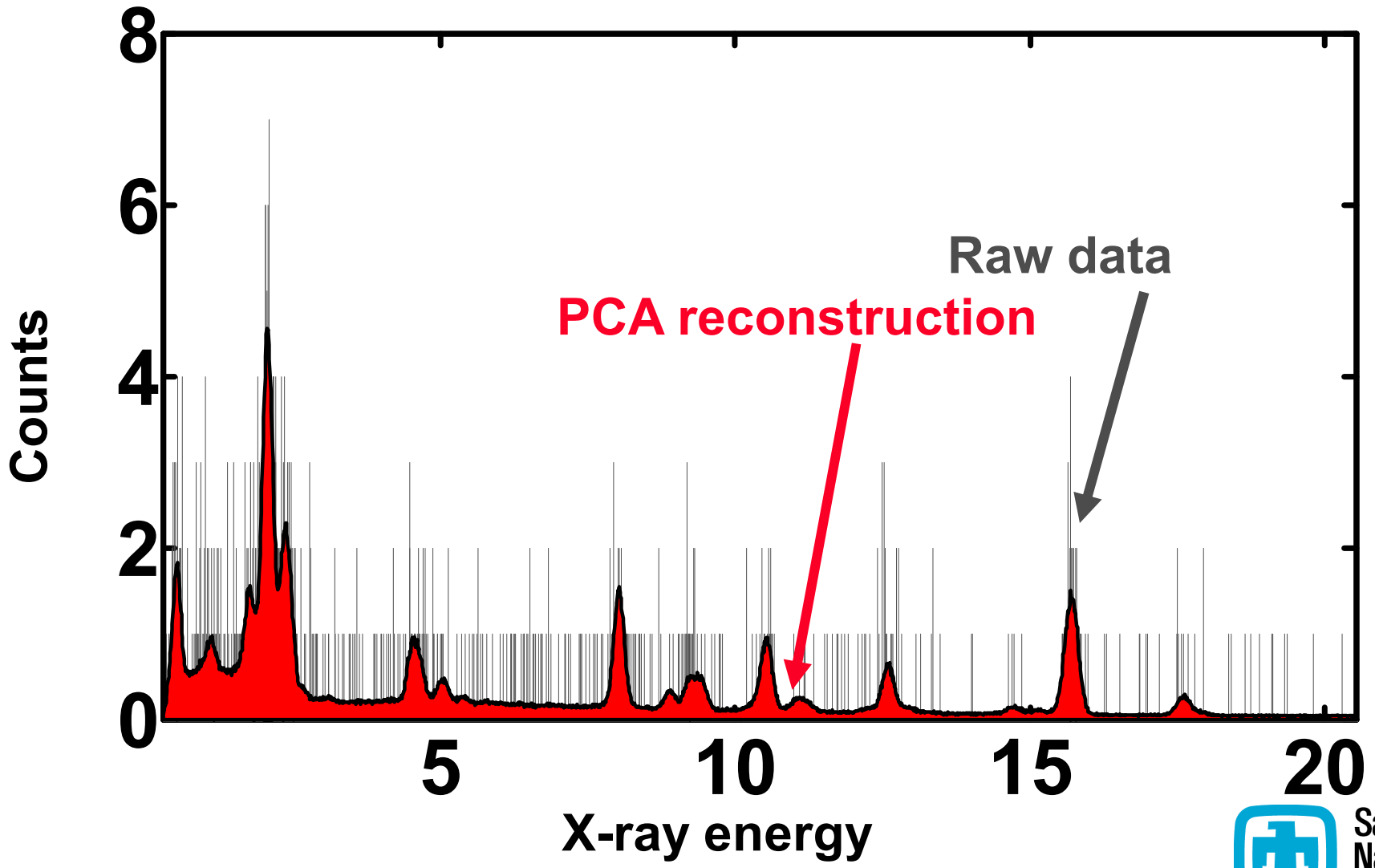
PCA produces a noise-filtered reconstruction of the data *at every pixel*



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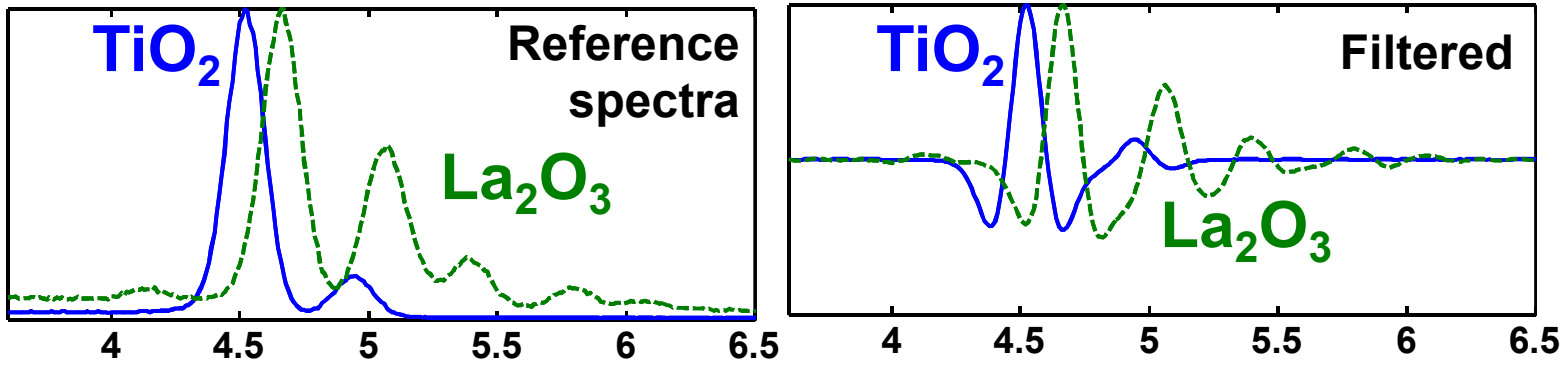
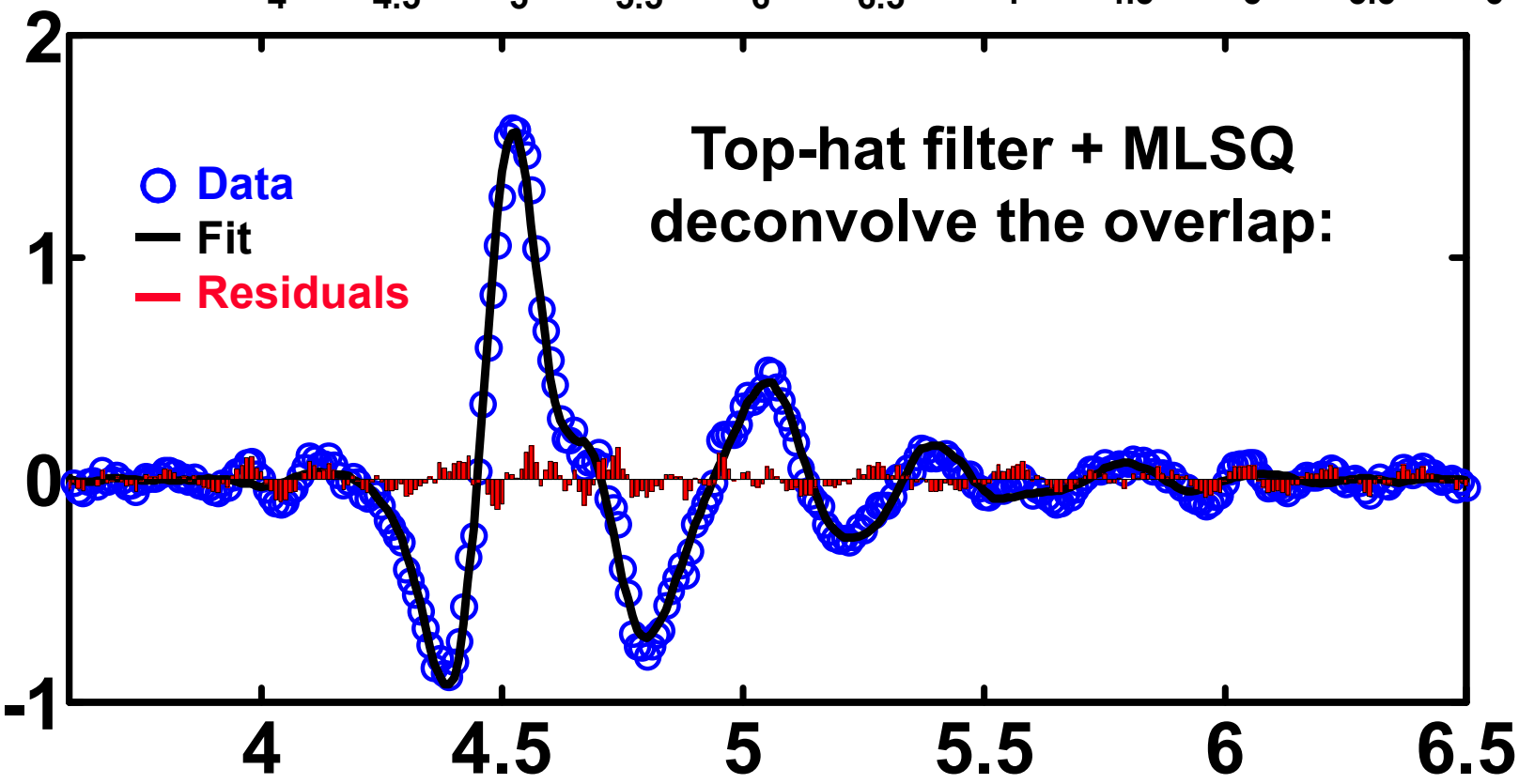
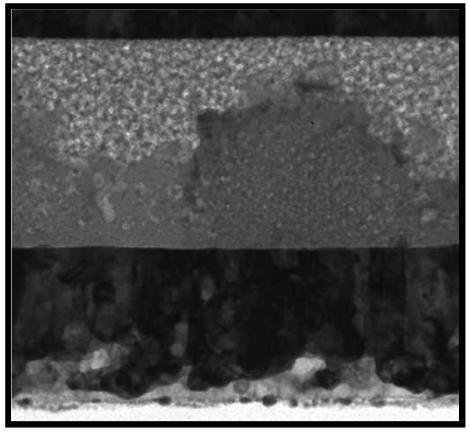
Noise-filtered spectra can be deconvolved and integrated

Ti K, La L overlap:

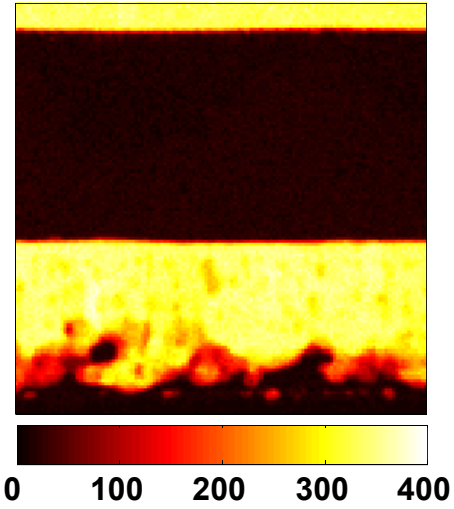




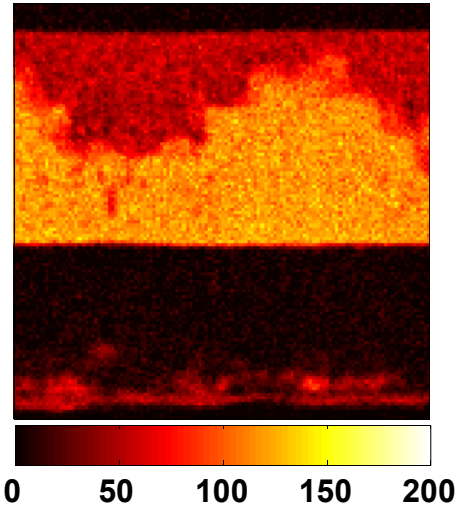
Integration and deconvolution at each pixel yields count-maps



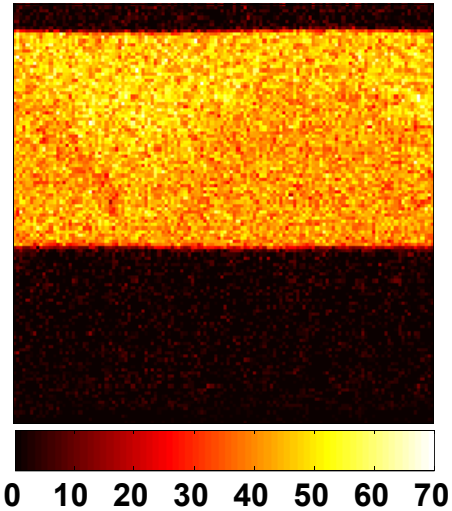
500 nm



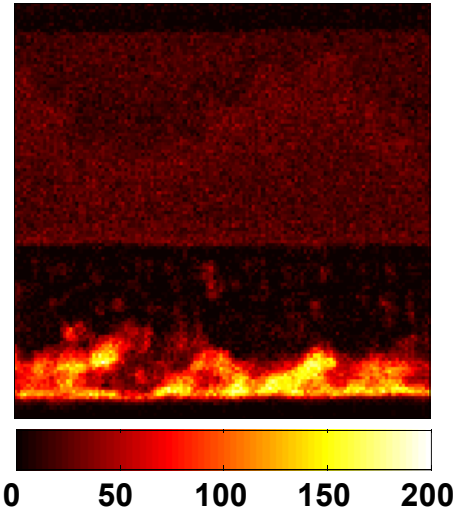
Pt counts



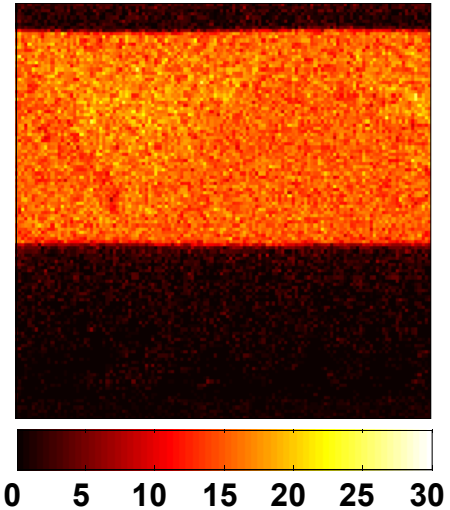
Pb counts



Zr counts



Ti counts



La counts

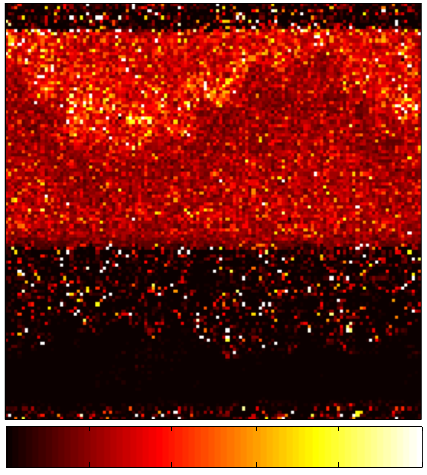
Count-maps and the Cliff-Lorimer equation yield quantitative maps

Cliff-Lorimer equation:

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

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

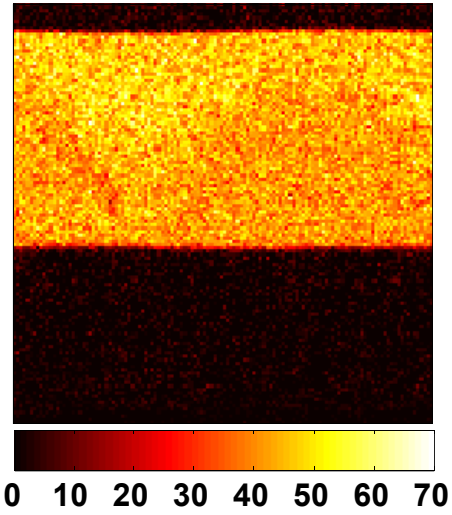
Quantitative mapping:



Zr/Ti cation ratio

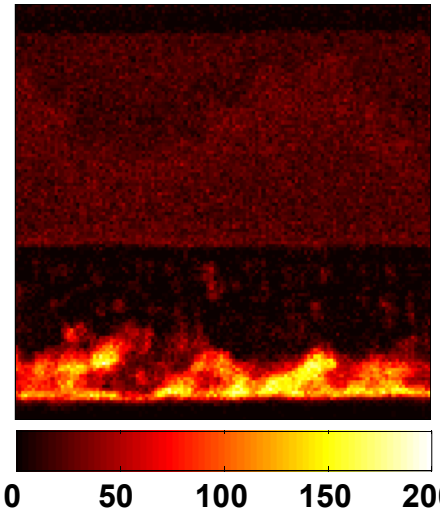
$= k_{ZrTi} \times$

1.203±0.075



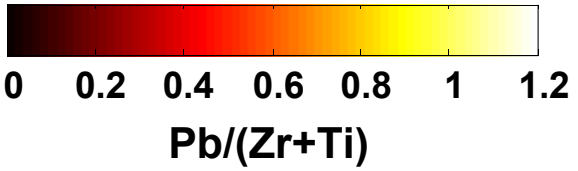
Zr counts

÷



Ti counts

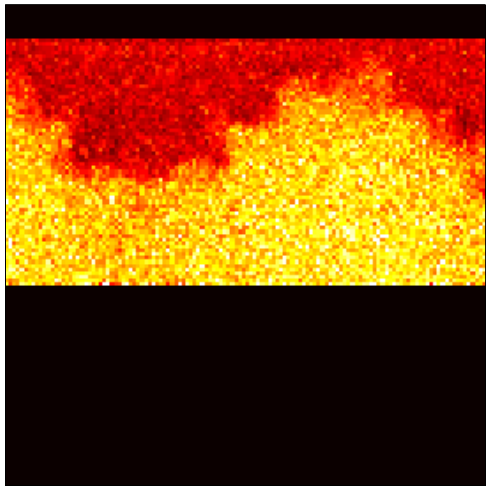
The overcoat+anneal process restores the Pb-stoichiometry

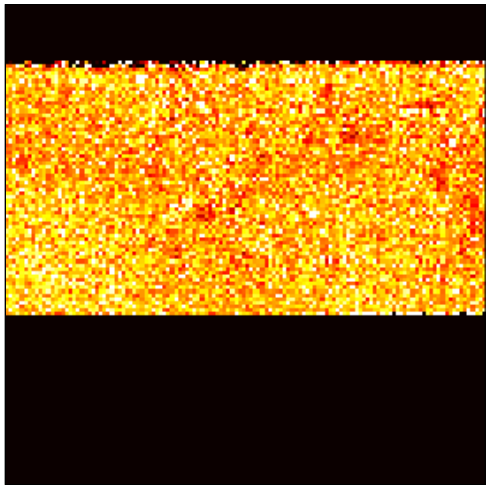


Mixed phase

Single phase

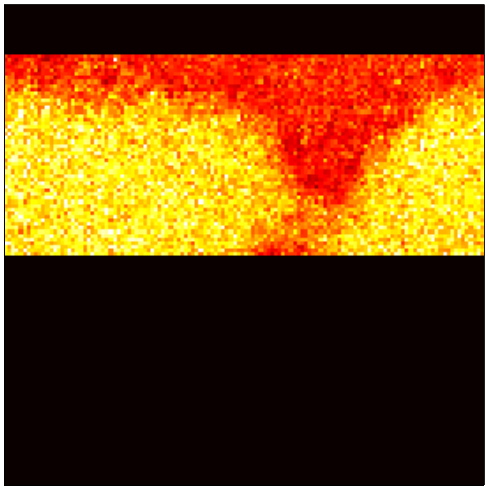
PLZT 12/70/30
650°C / 30 min

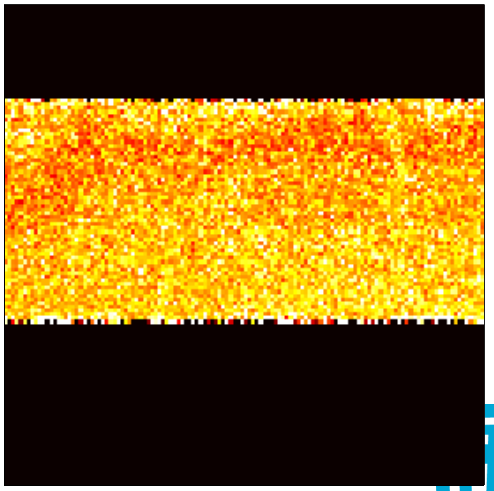




200 nm

PZT 53/47
650°C / 30 min





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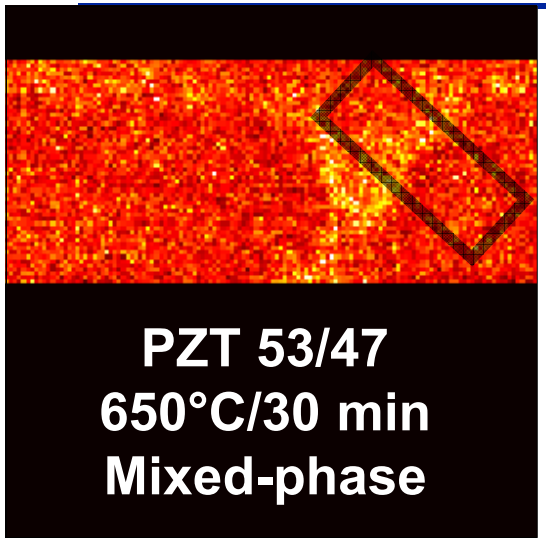
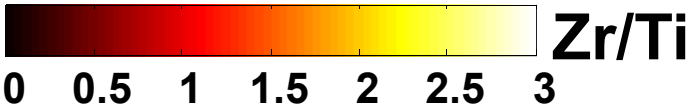
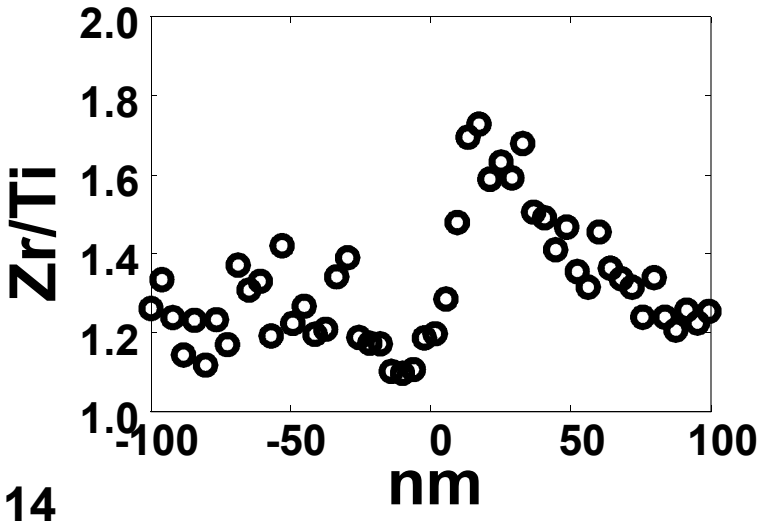
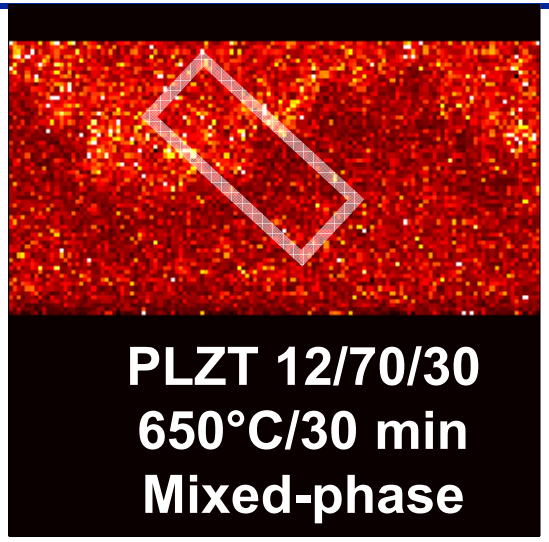
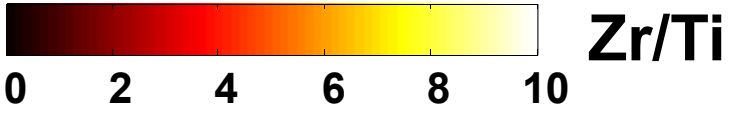
Zr segregates to the fluorite

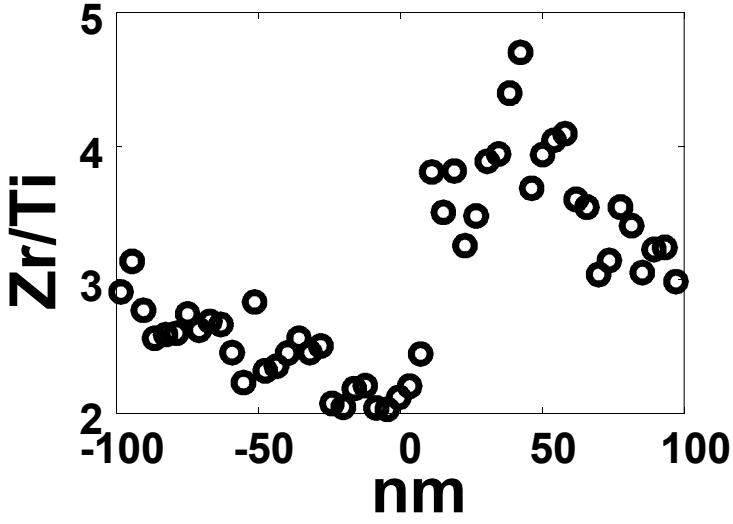




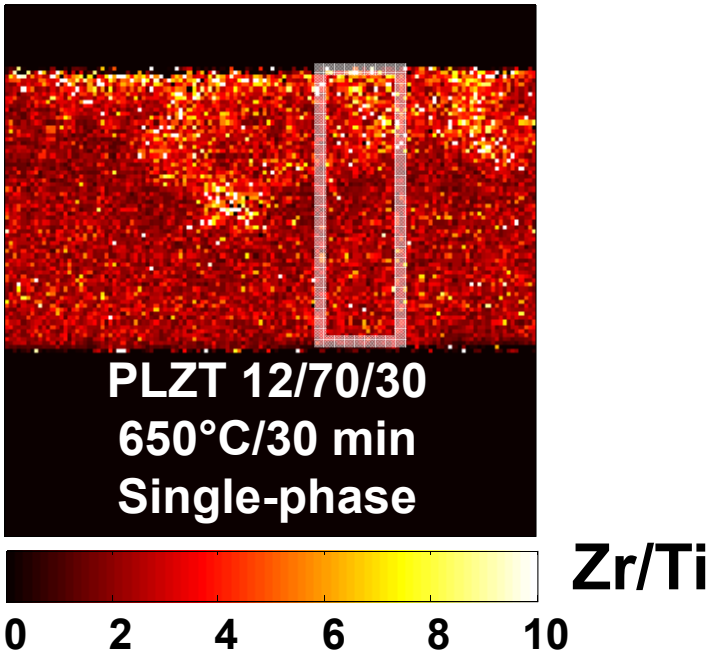


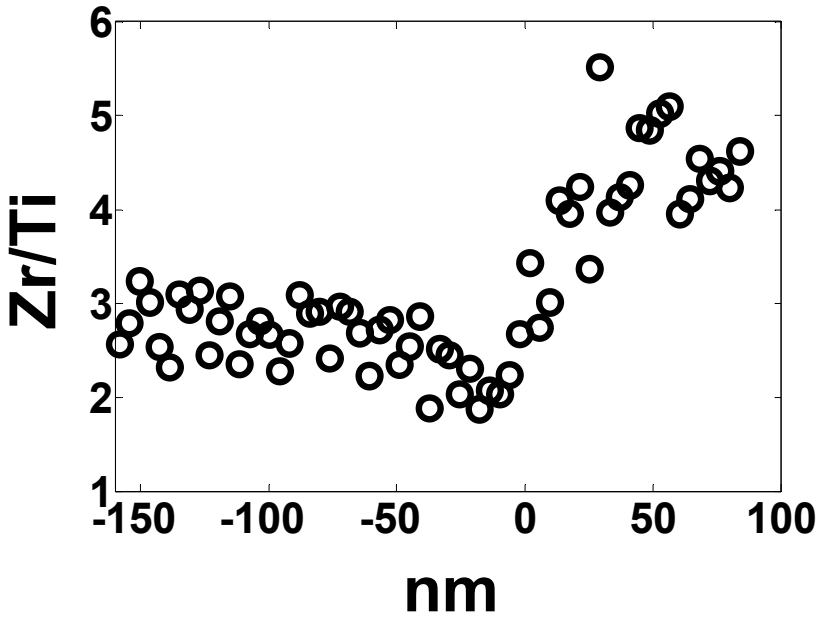






Zr segregation remains after the fluorite → perovskite conversion





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

→Currently under investigation

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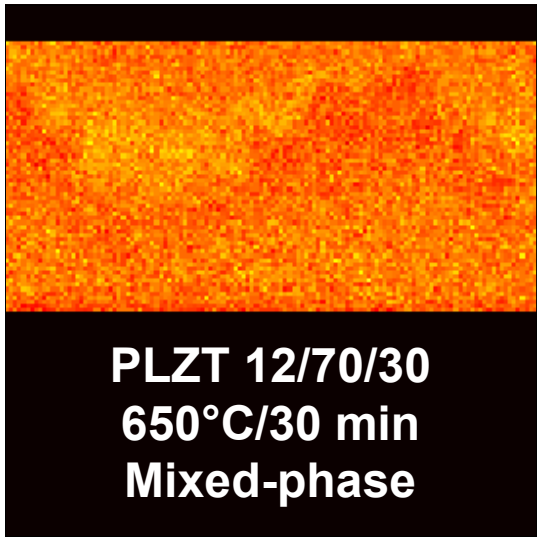
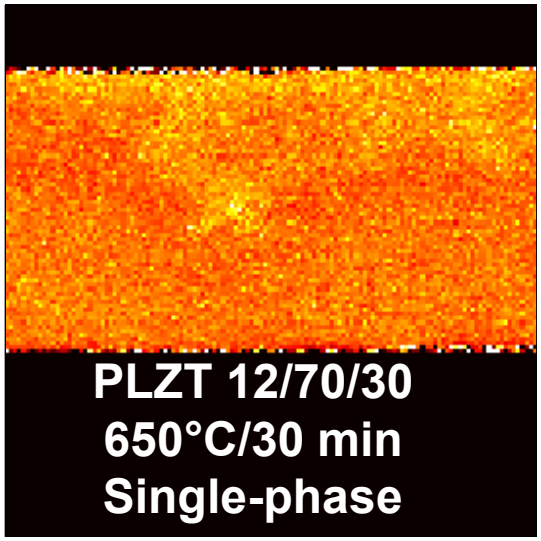
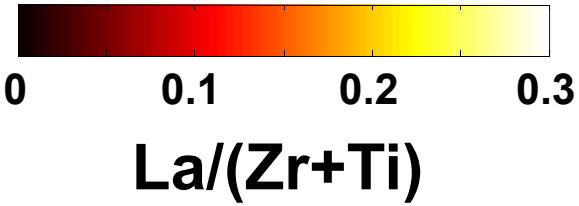
La segregation is also present







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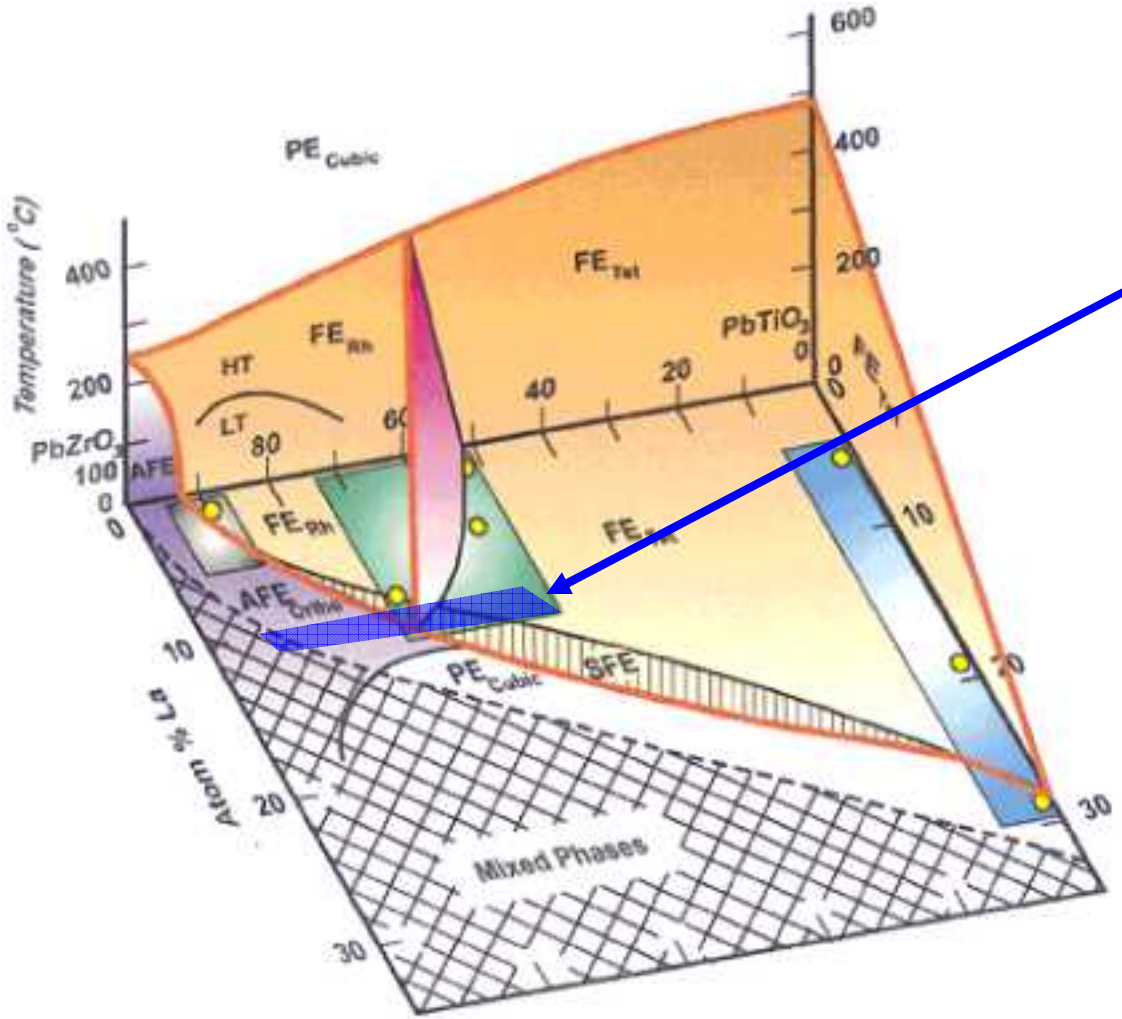
Accurate measurement of cation content is important to interpret properties



Measured chemistry crosses phase boundaries –

This may degrade properties

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

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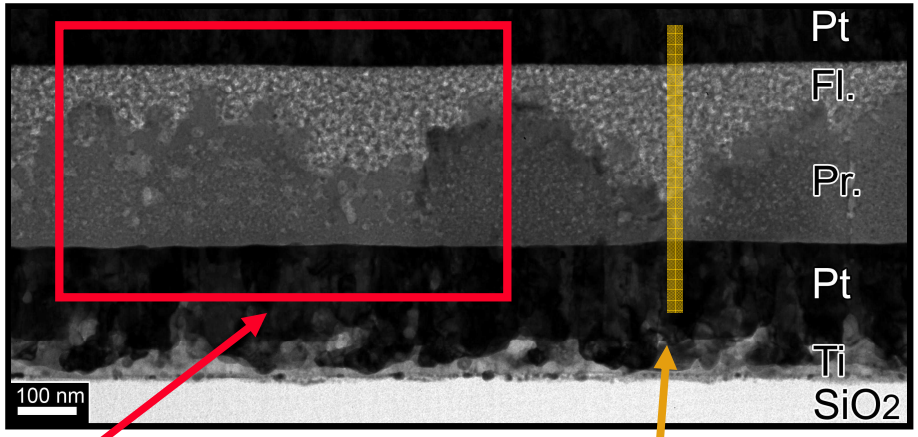
We have succeeded in mapping cations at a length scale ≈ feature size

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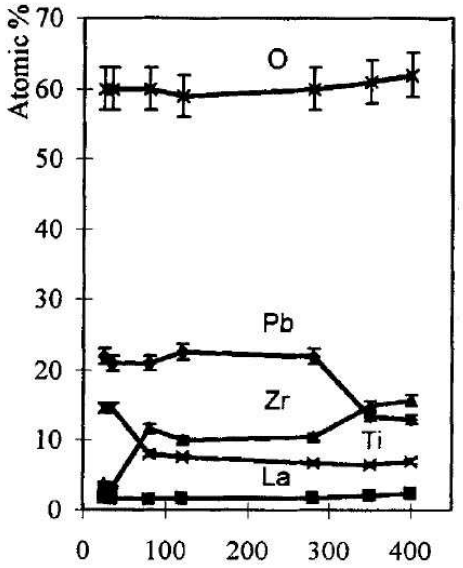
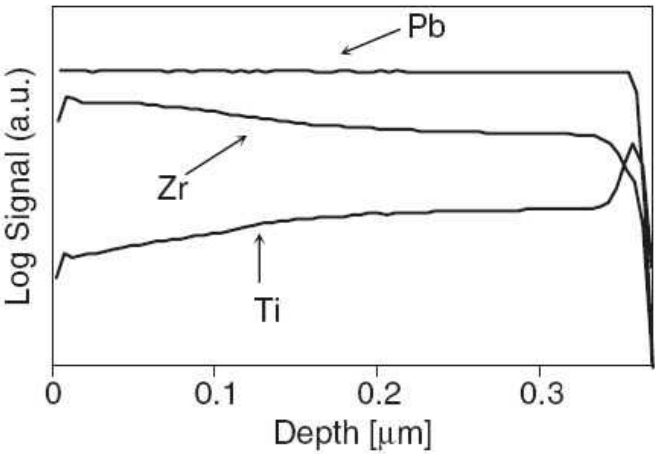
We have succeeded in mapping cations at a length scale ≈ feature size

EDS linescan:
Spot size ~10 nm



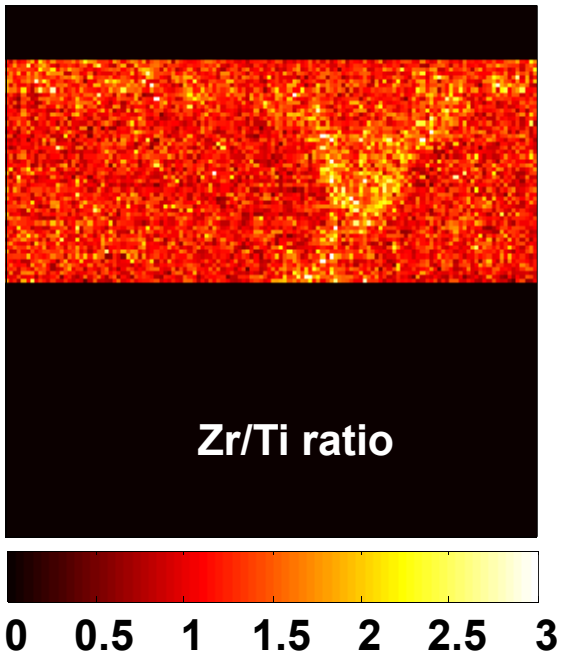
Drazic & Kosec, Ferroelectrics, V201, P.23, 1997

SIMS depth-profile:
Sampled area 40×40 μm



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

Quantified SI:
500×250 nm



Parish et al., J. Am. Ceram. Soc., submitted

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