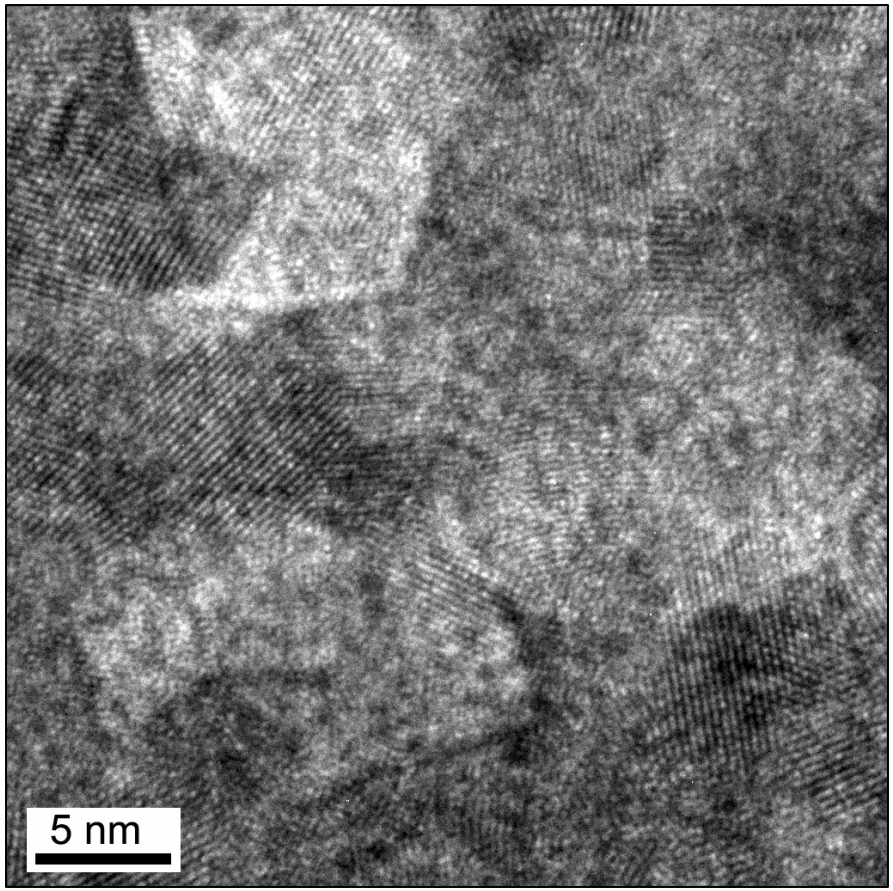
SAND2007-6166C

# Phase reversibility in $(Pb,La)(Zr,Ti)O_3$ thin-film ferroelectrics studied by transmission electron microscopy

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National Nuclear Security Administration

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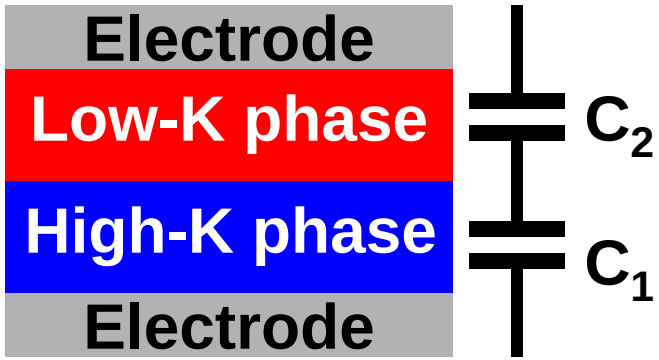
# Thin-film P(L)ZT ferroelectrics are important for capacitor applications

**$Pb(Zr,Ti)O_3$ and $(Pb,La)(Zr,Ti)O_3$ are high-dielectric-constant (K) ferroelectrics that can be formed into multilayer thin films**

**→Referred to as PZT and PLZT**

**Multiple phases can form during processing – these act as series capacitors**

**→ Loss of overall capacitance of device**



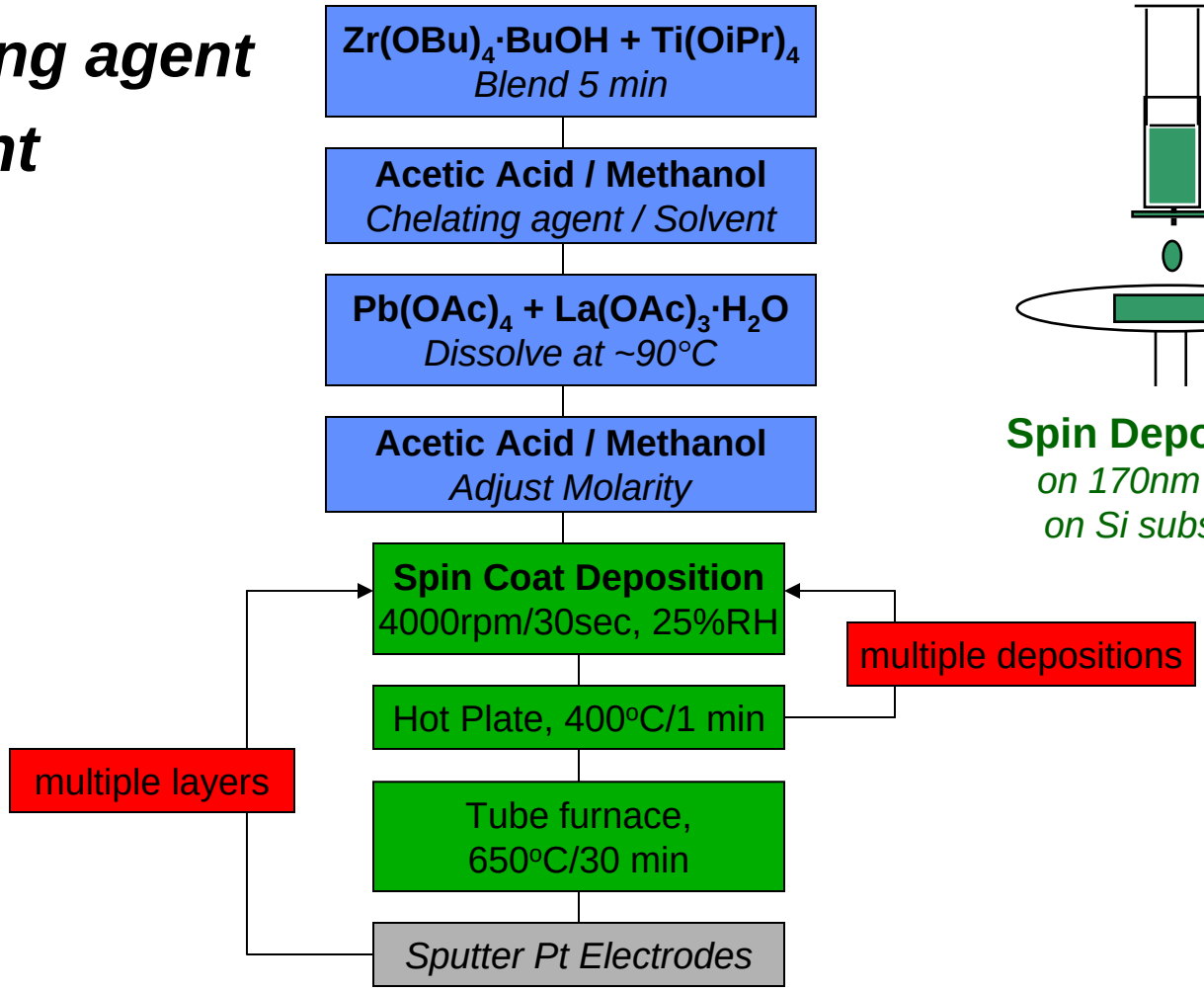

$$C_{TOTAL} = \frac{1}{\frac{1}{C_1} + \frac{1}{C_2}}$$

**Lowest capacitance value dominates device performance!**

# We used chemical solution deposition to make P(L)ZT thin films

**HOAc = *chelating agent***

**MeOH = *solvent***






**Spin Deposition**
*on 170nm Pt//Ti*
*on Si substrate*

*R.A. Assink and R.W. Schwartz;* ***Chem. Mater.****, [5], 511 (1993).*

*G. Yi and M. Sayer;* ***J. Appl. Phys****. [64] 2717 (1988).*

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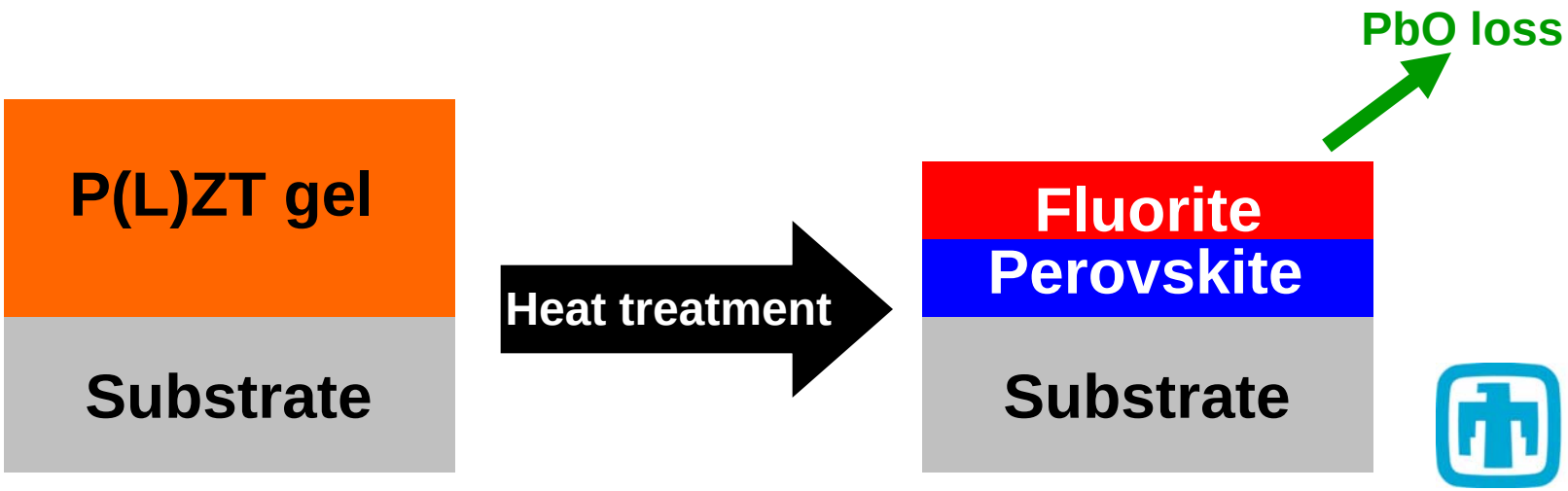
# PbO volatility can result in poor film quality

- Only the perovskite phase of P(L)ZT has a high dielectric constant 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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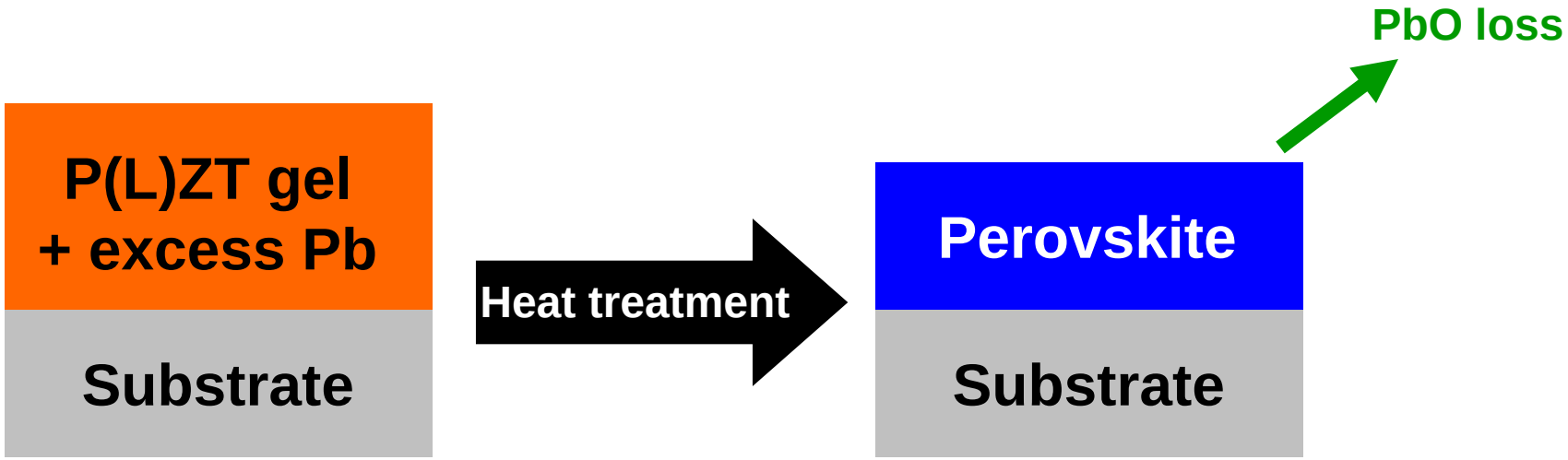
# Excess Pb avoids fluorite formation, but has detrimental effects

**Typically, 10-20% 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 without excess Pb?**

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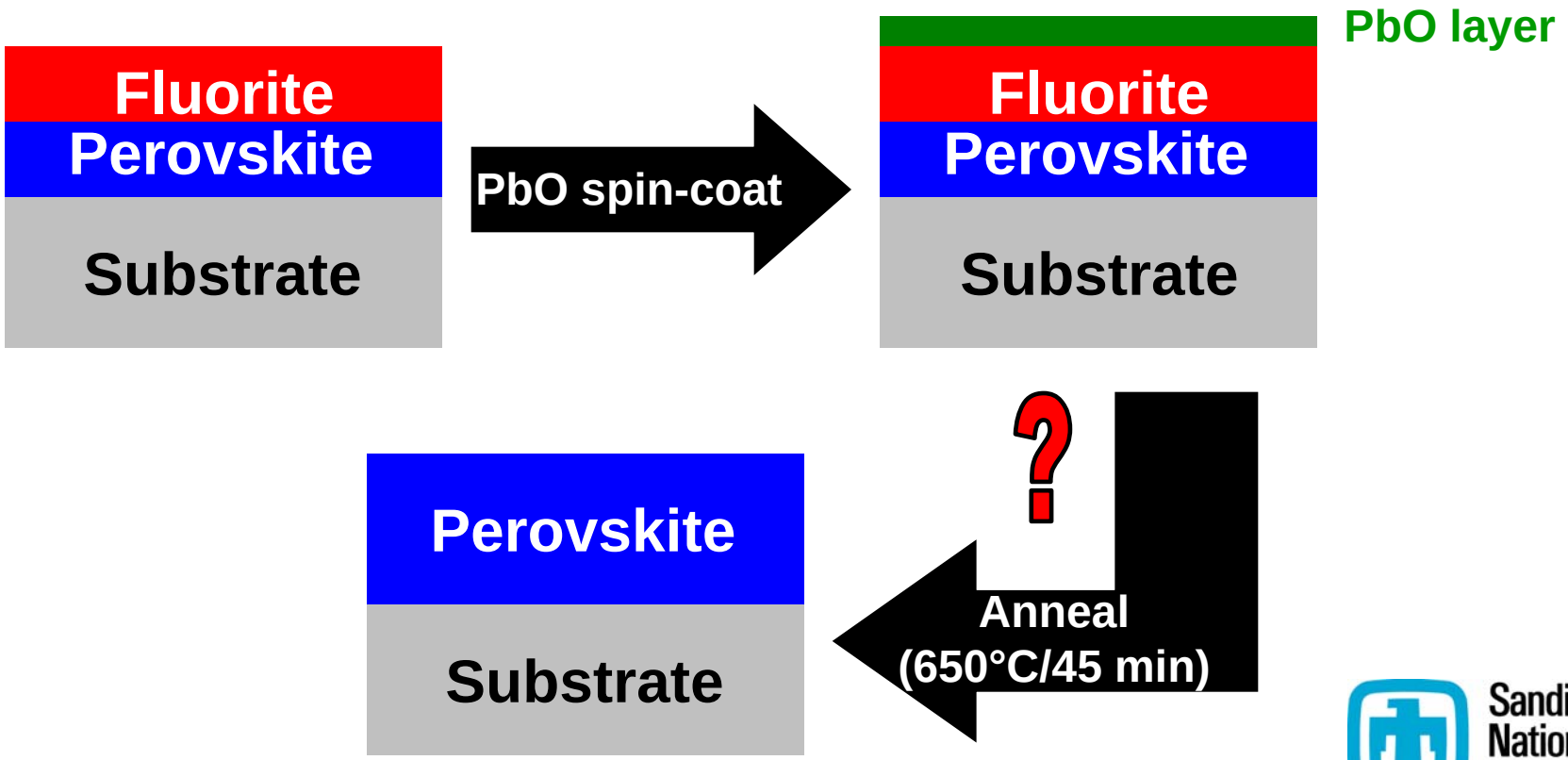
# Will annealing crystallized films under a PbO solution restore the desired phase?

***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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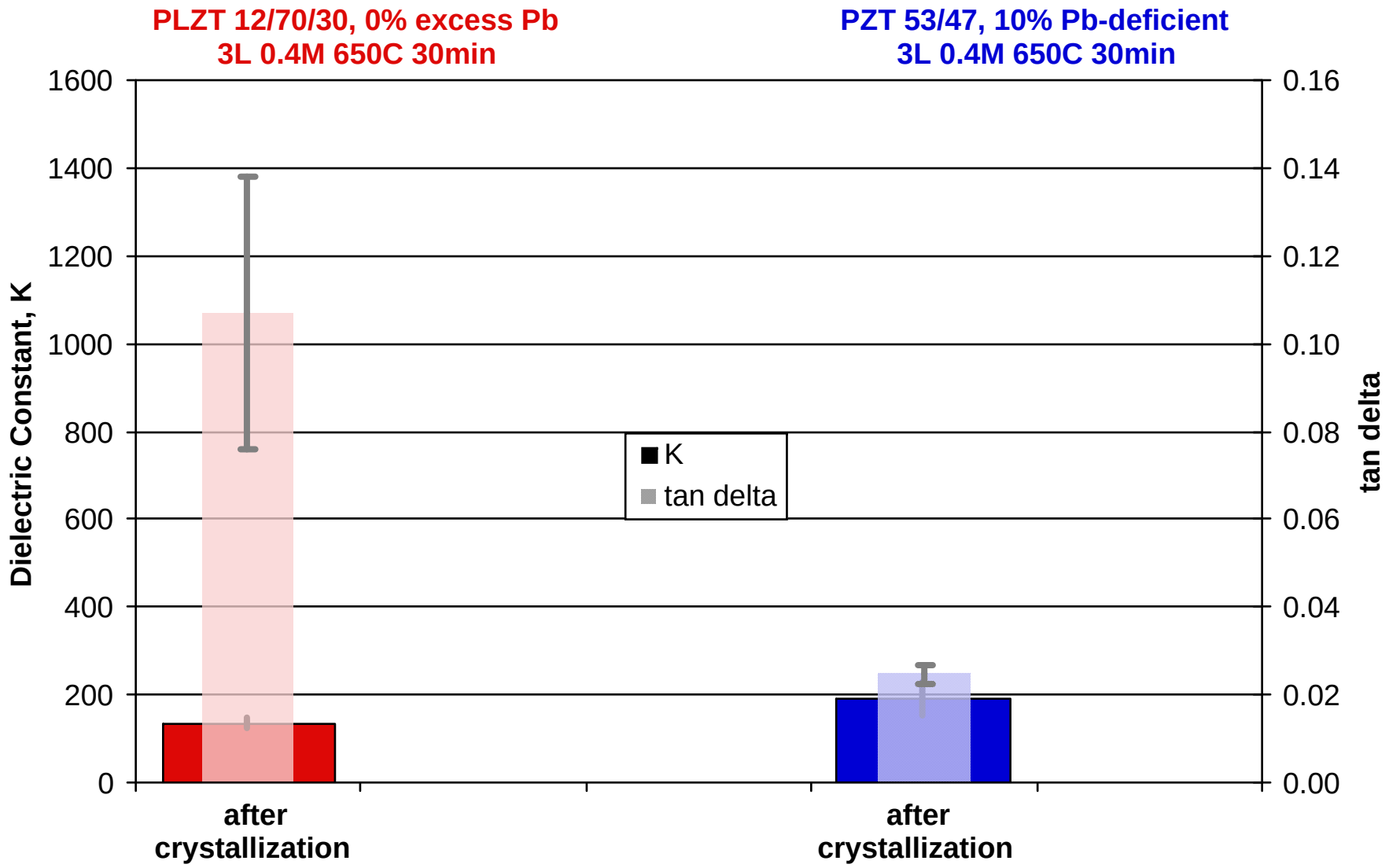
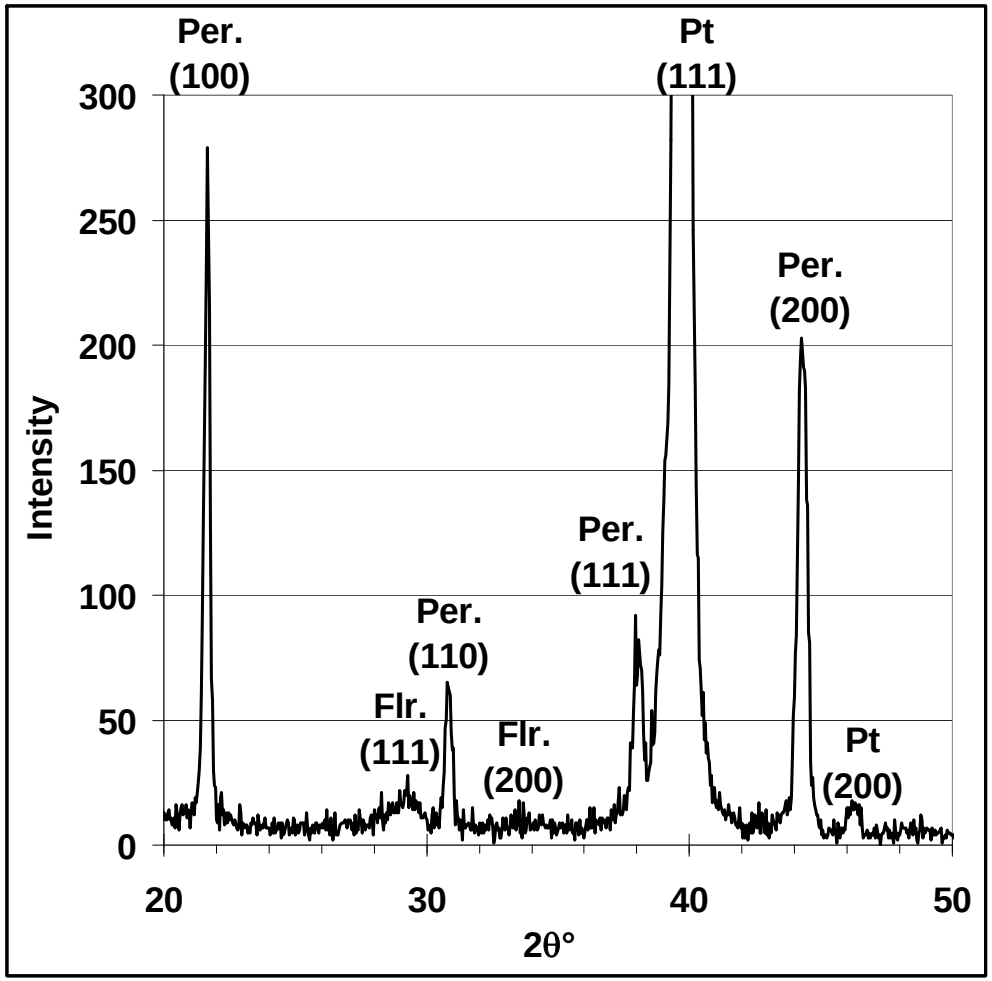
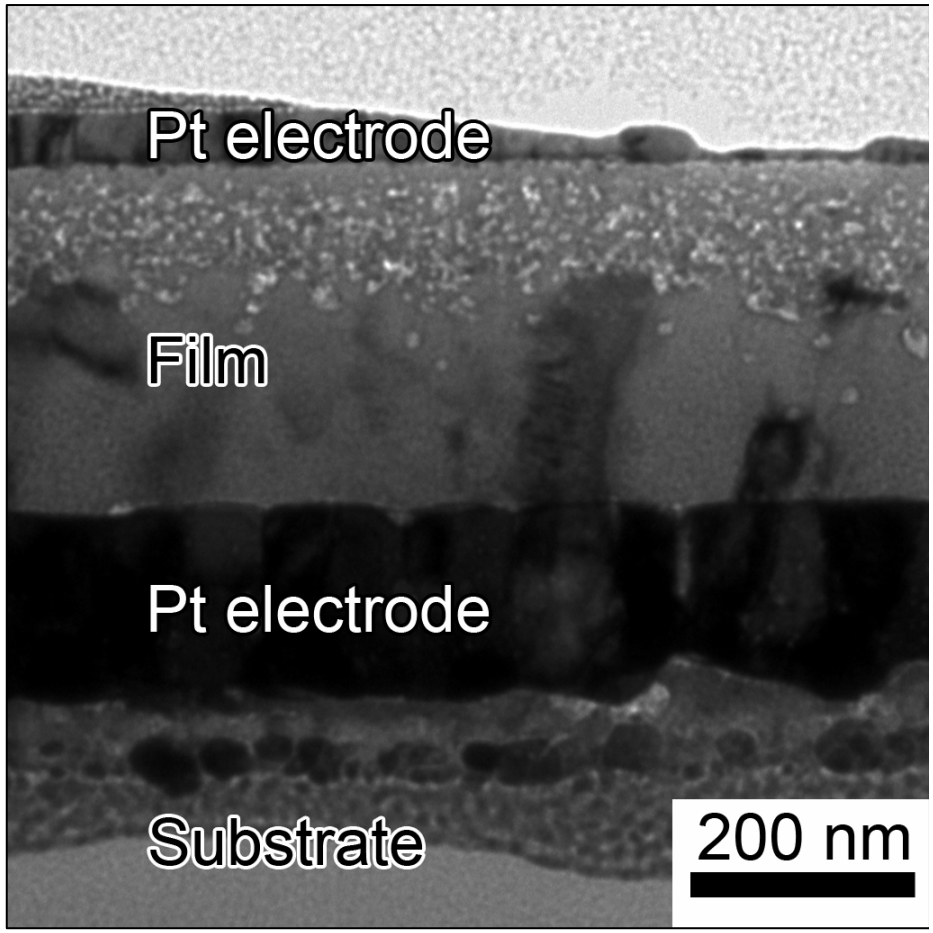
# As-crystallized films show poor dielectric properties (K=100~200)



# As-crystallized films show mixed-phase structure in XRD and TEM




**PLZT 12/70/30**

**Per. = Perovskite**
**Flr. = Fluorite**

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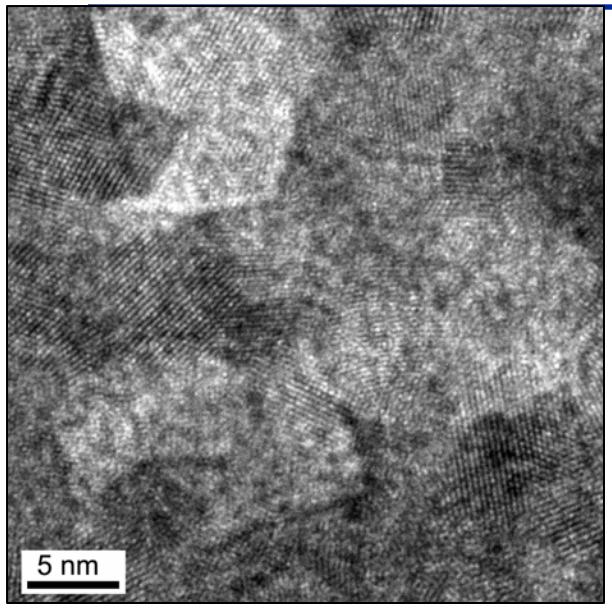
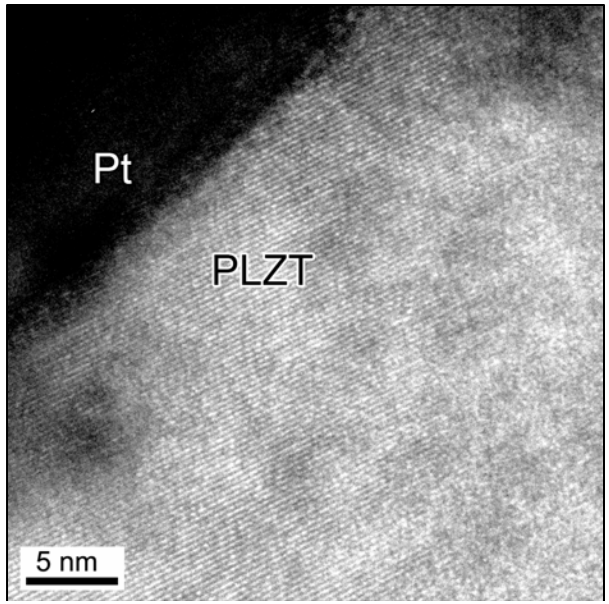
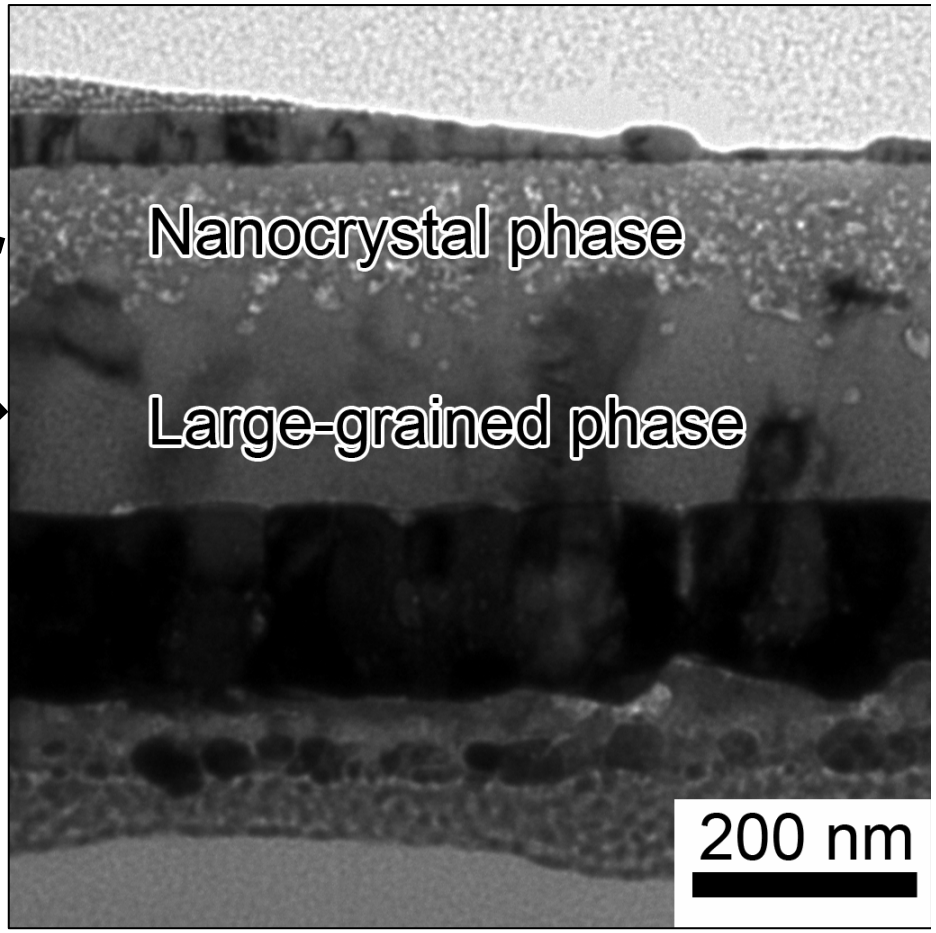
# High-resolution TEM shows crystal structure




**PLZT 12/70/30**

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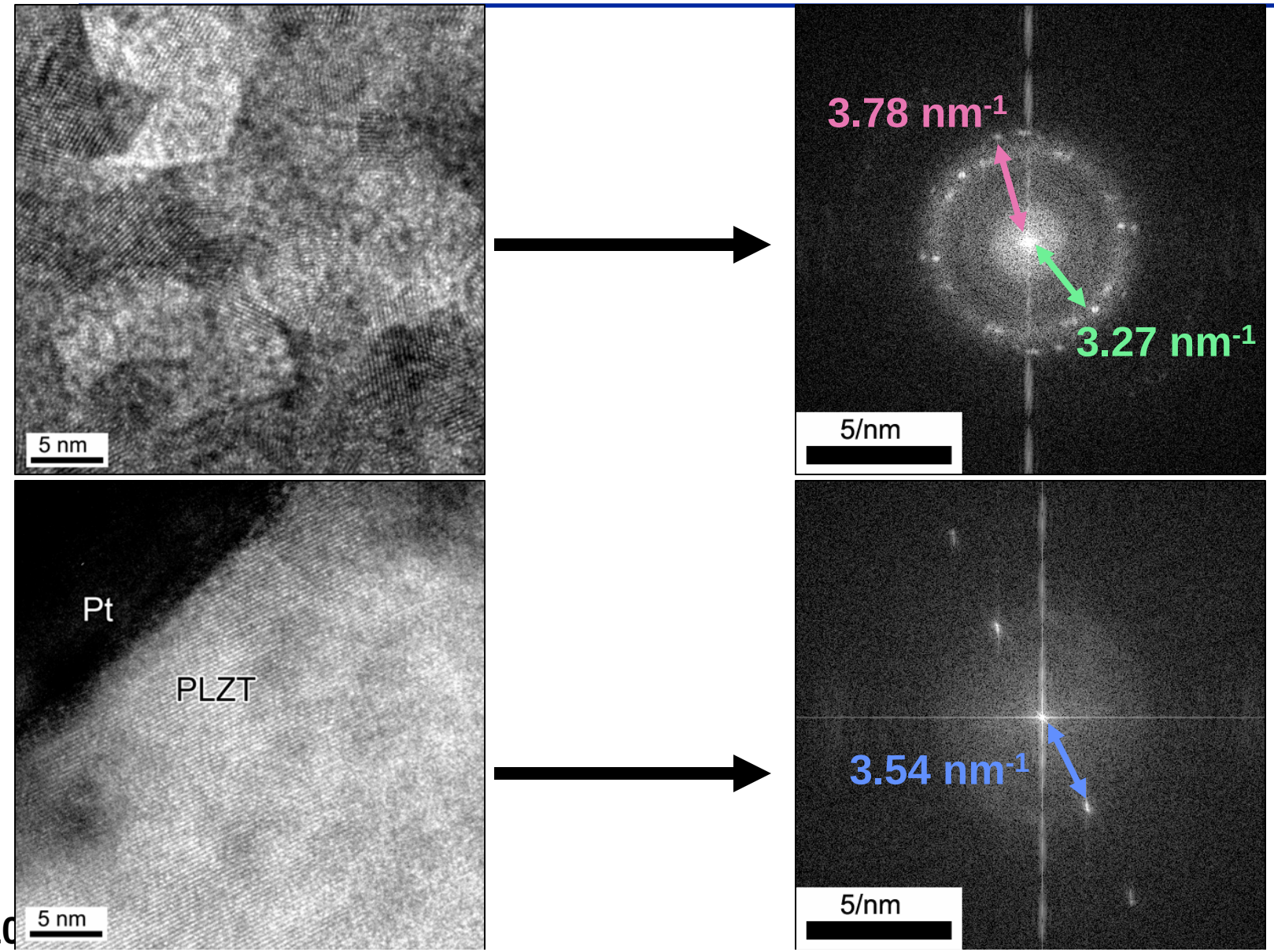
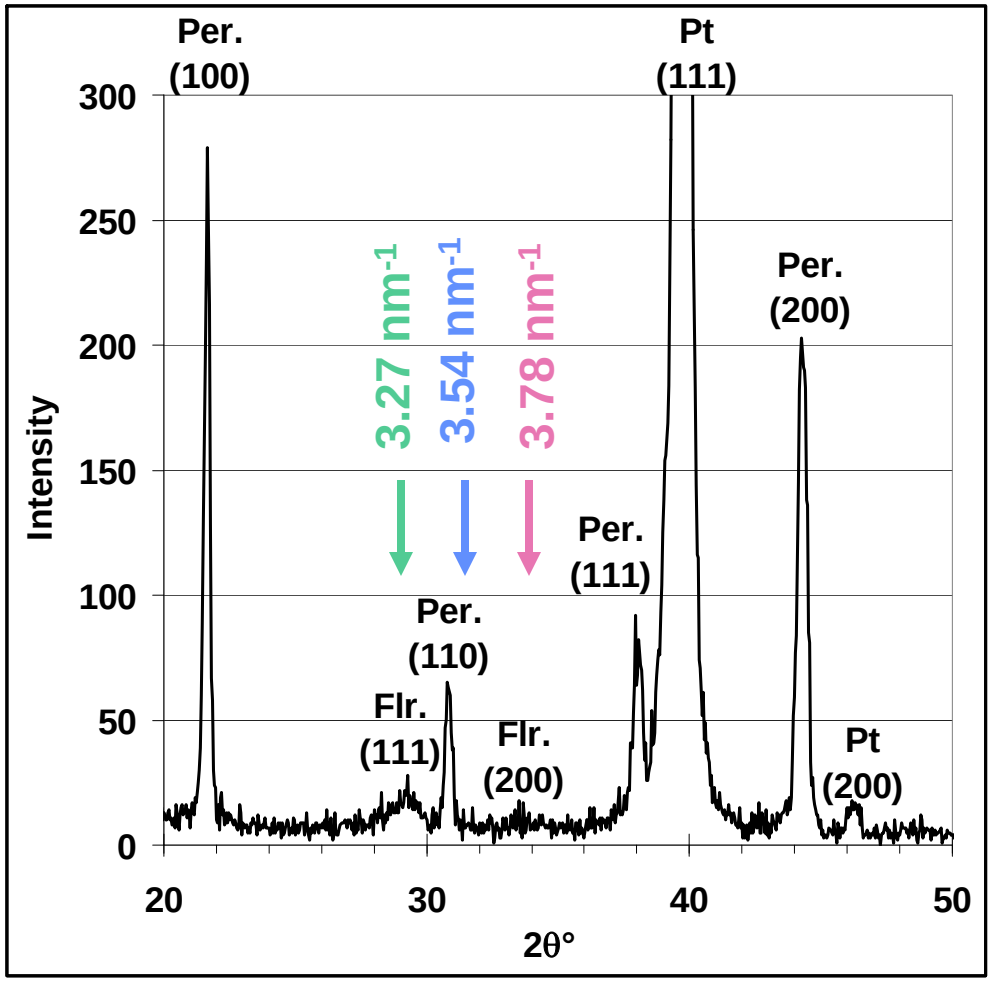
# Fourier transforms allow lattice spacings to be determined



# TEM lattice spacings match XRD data

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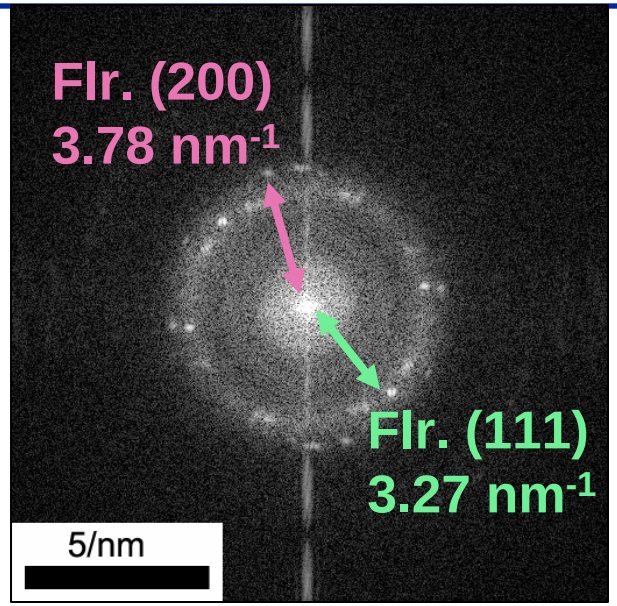
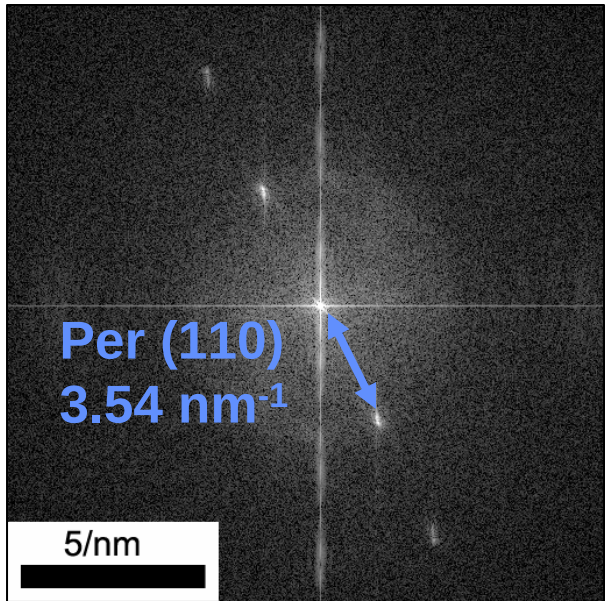
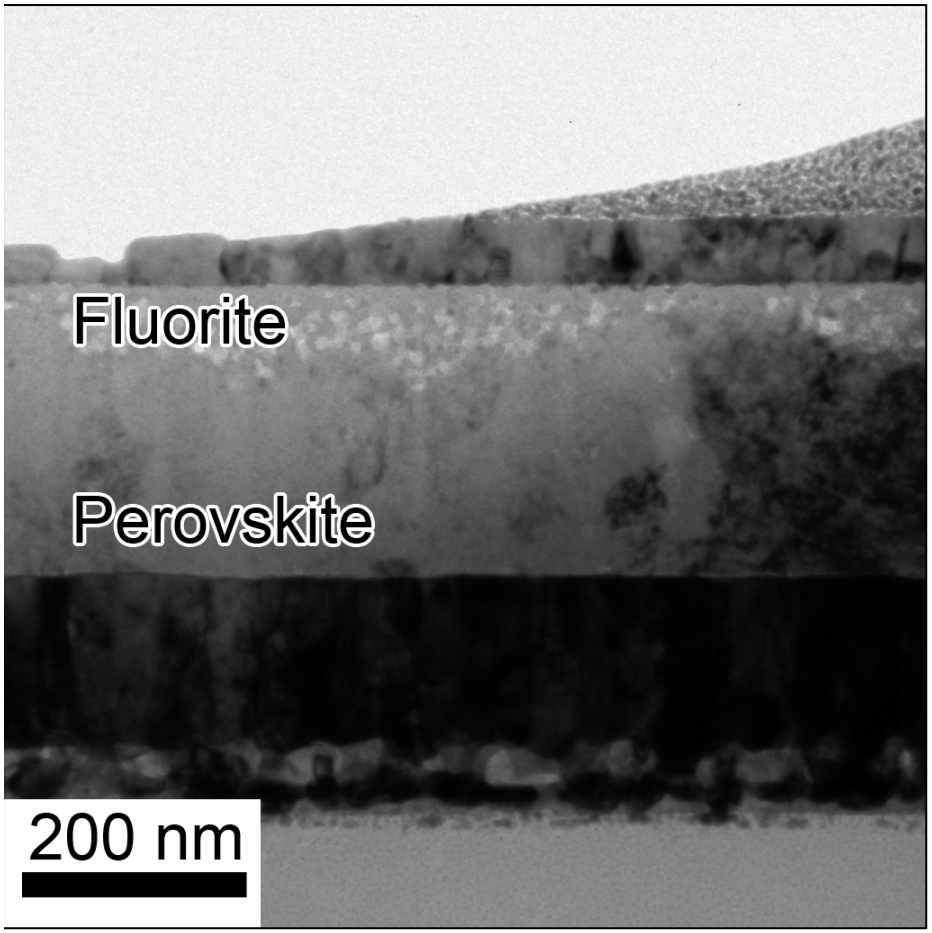
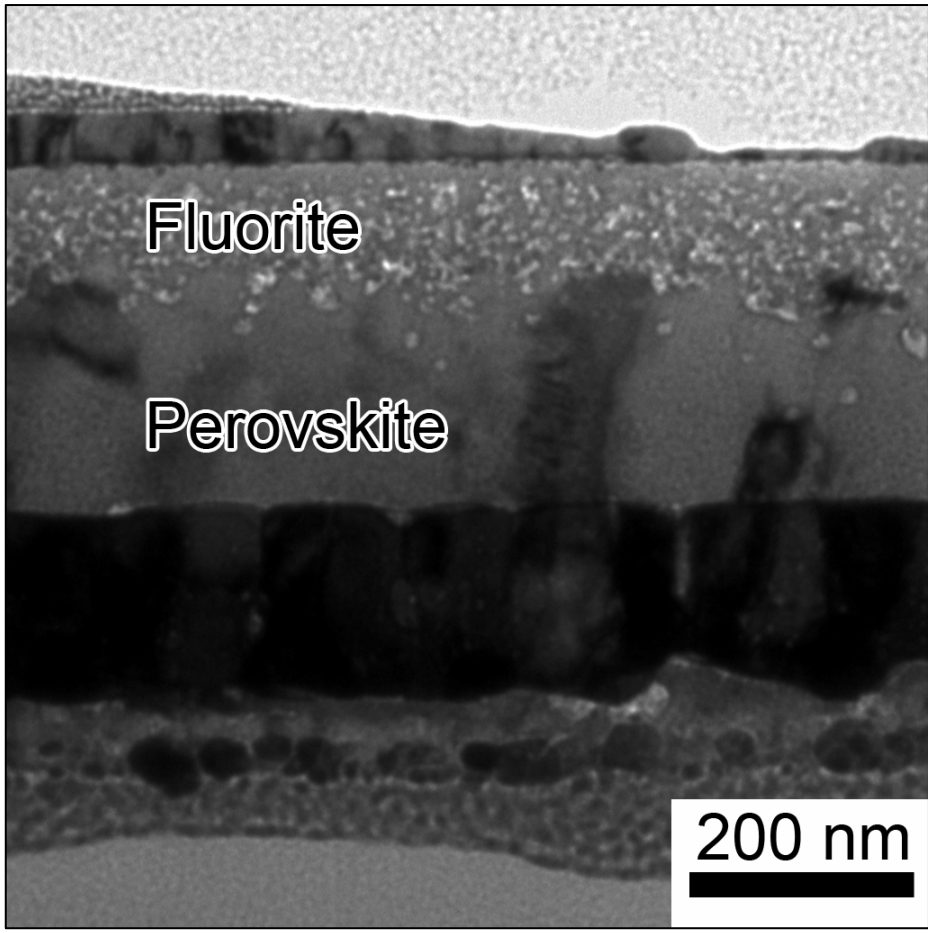


# As-crystallized samples suffer from surface fluorite formation




PZT 53/47




PLZT 12/70/30

*→Causes poor dielectric properties (K=100~200)*

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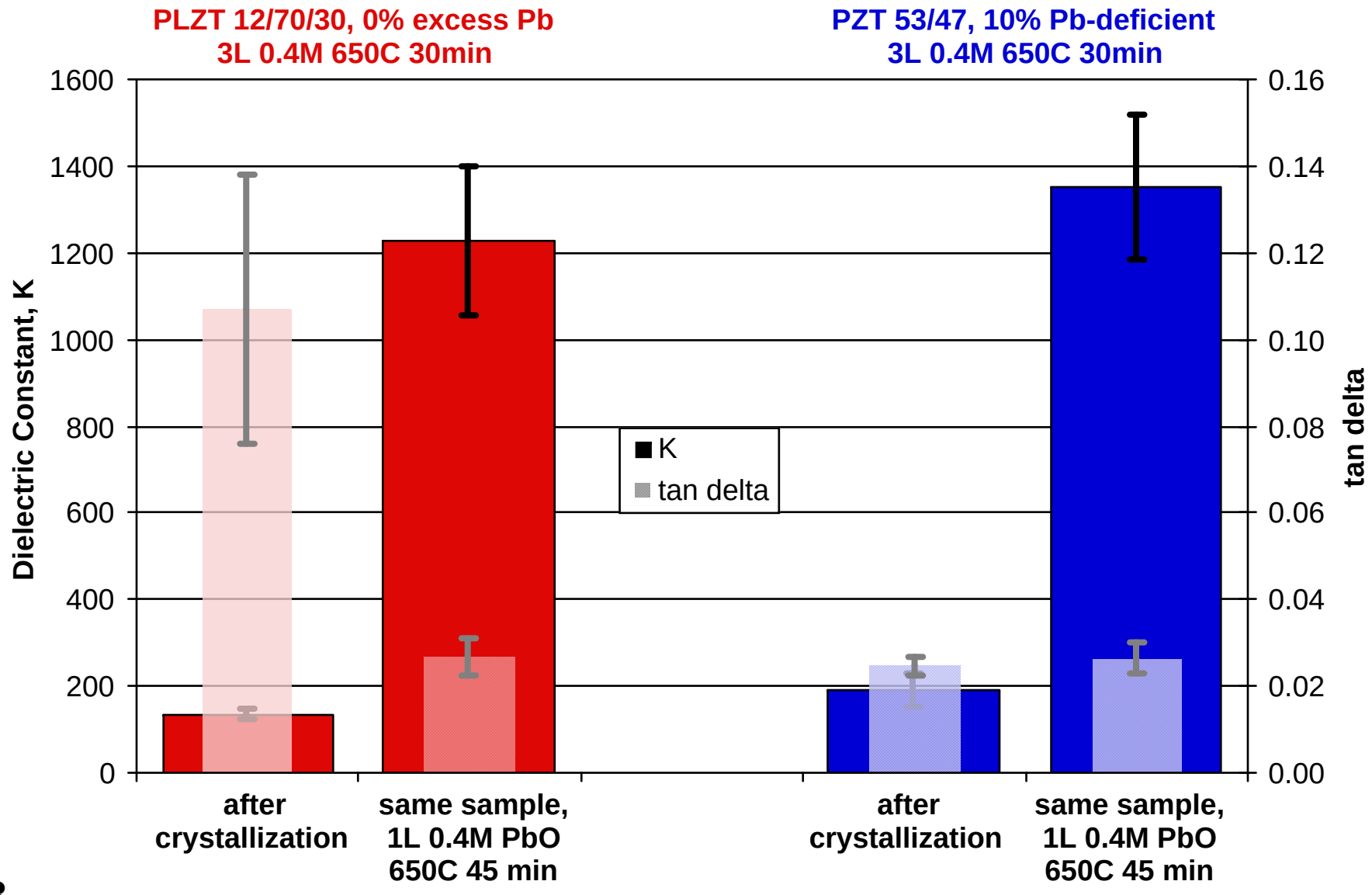
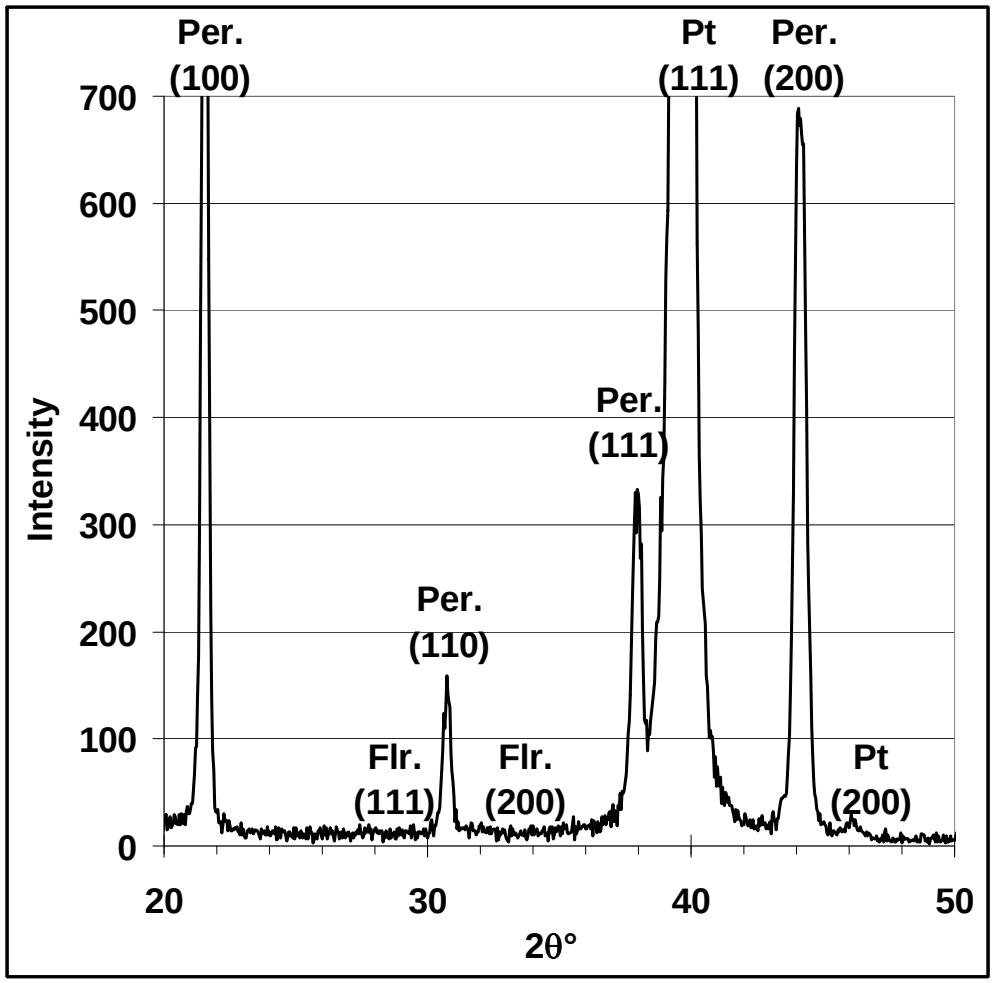
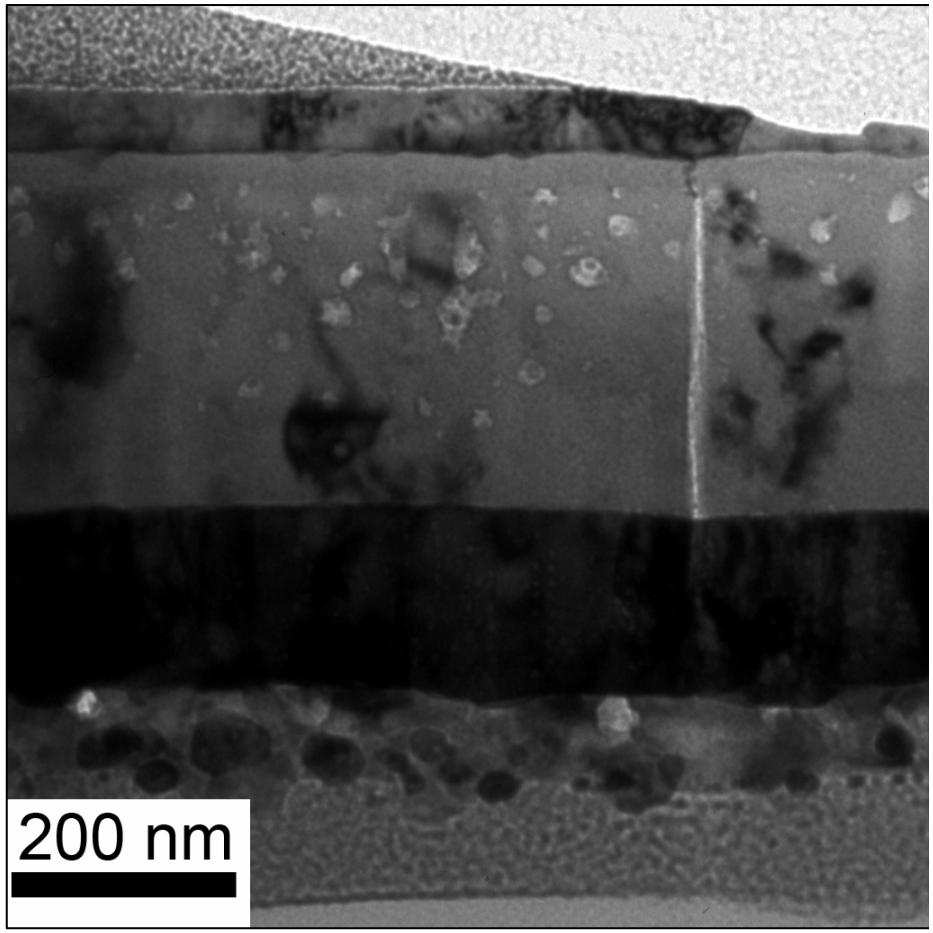
# Overcoated + annealed films show improvement in dielectric properties (K>1000)



# After overcoating + annealing, XRD and TEM show a single-phase material




PLZT 12/70/30

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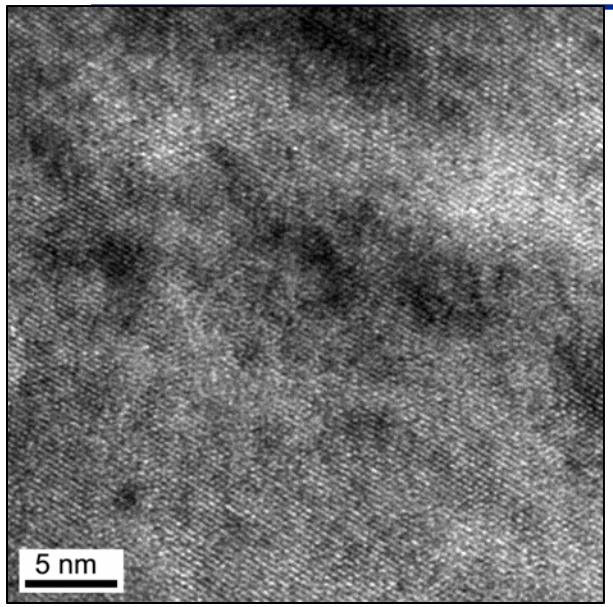
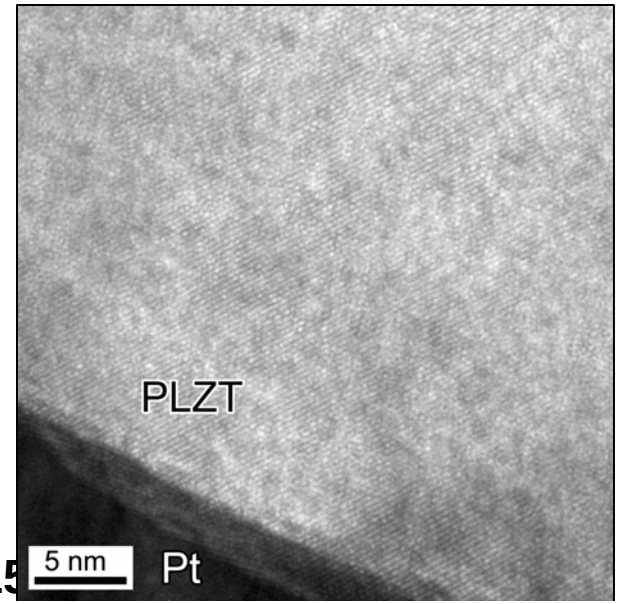
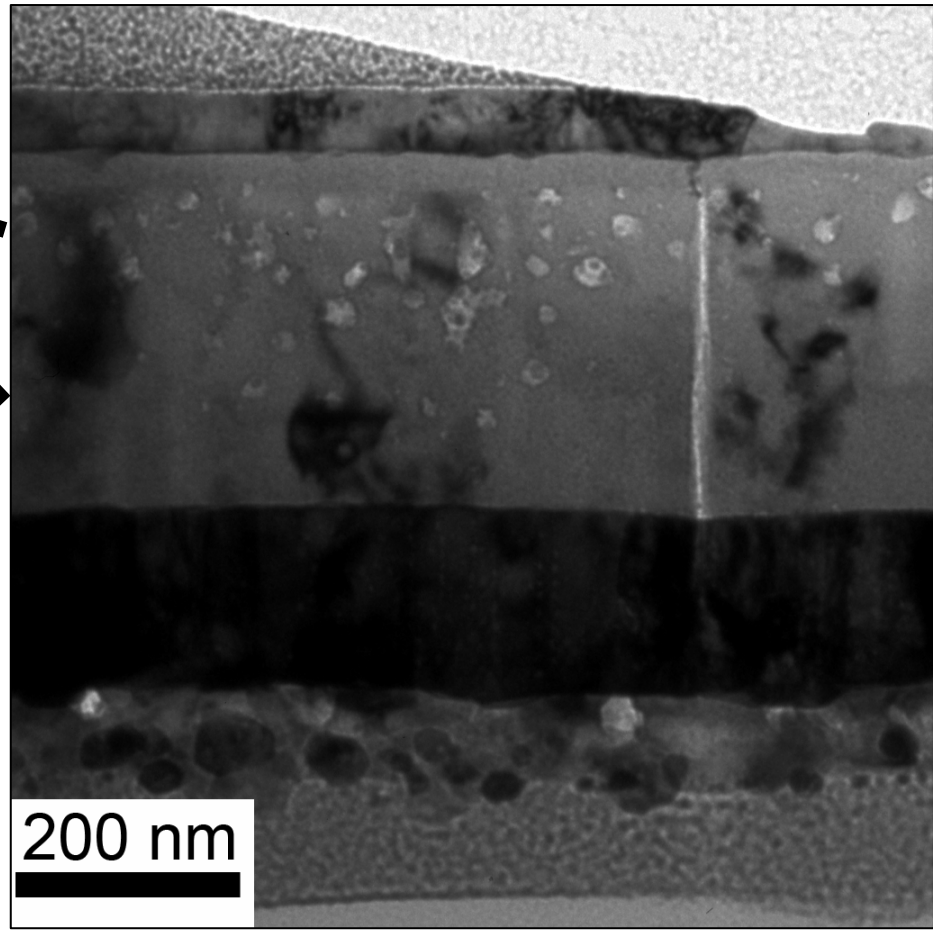
# High-resolution TEM shows crystal structure




**PLZT 12/70/30**

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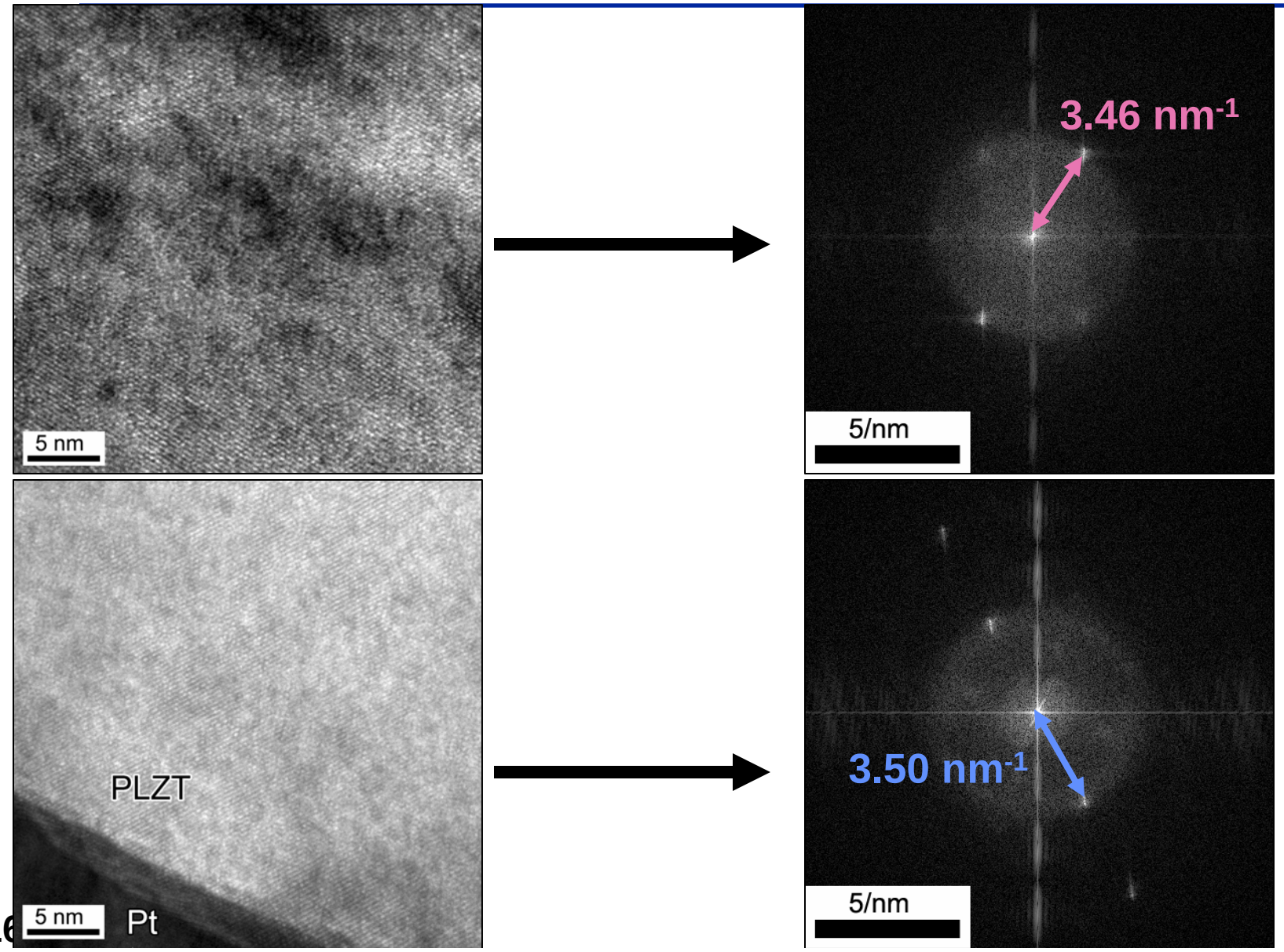
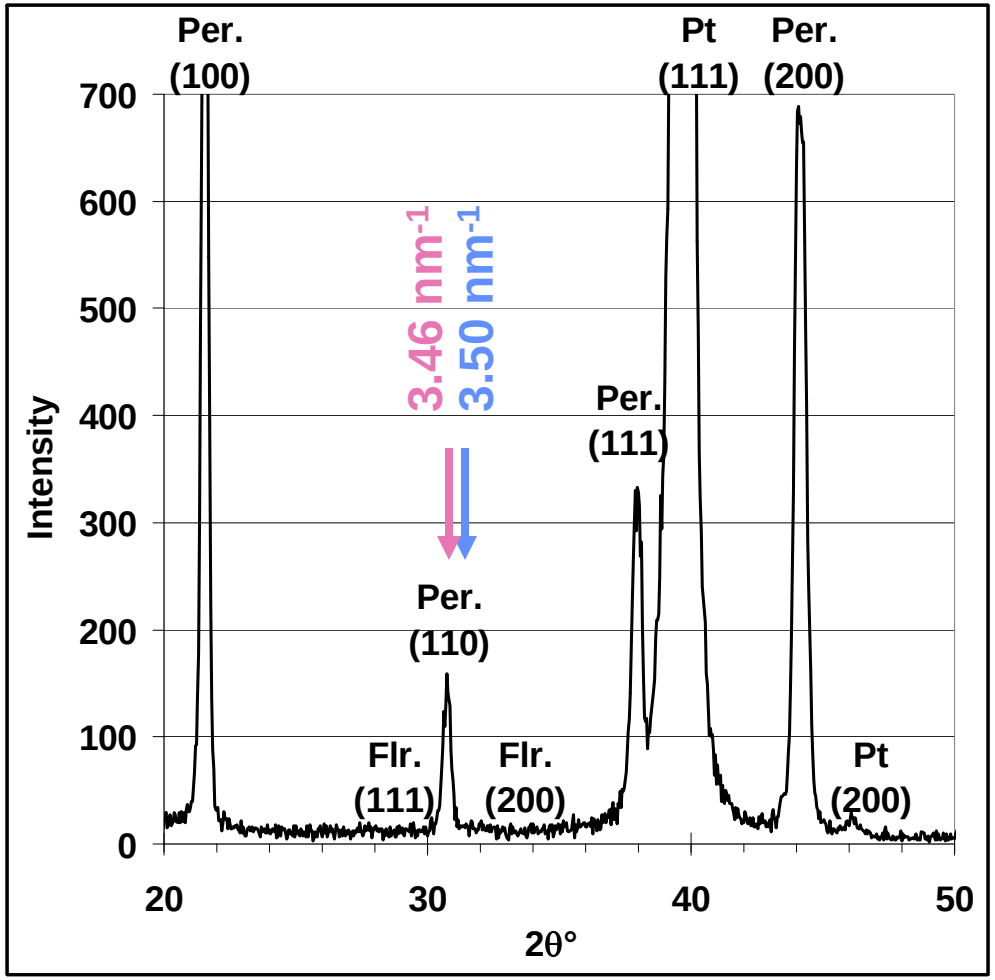
# Fourier transforms allow lattice spacings to be determined



# TEM lattice spacings match XRD data

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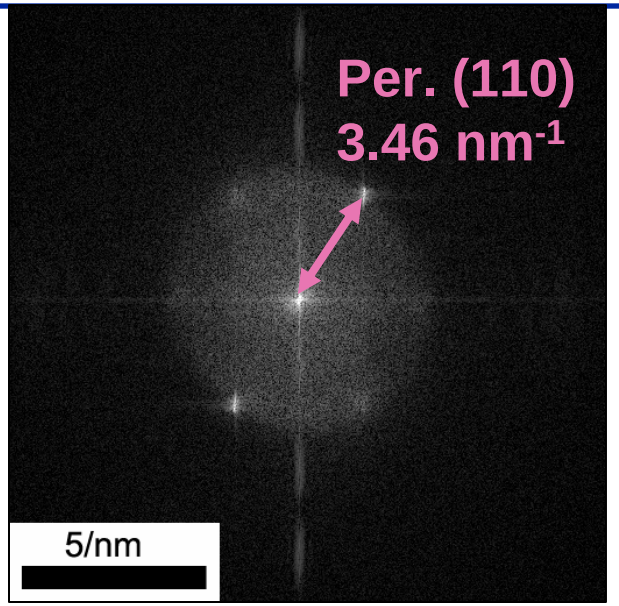
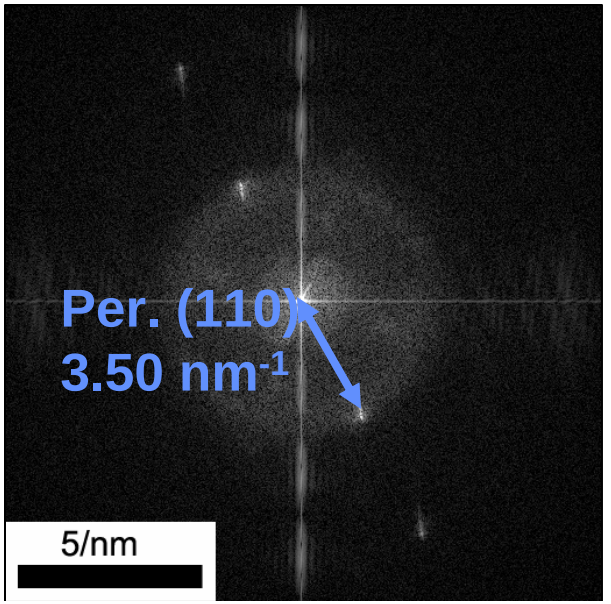
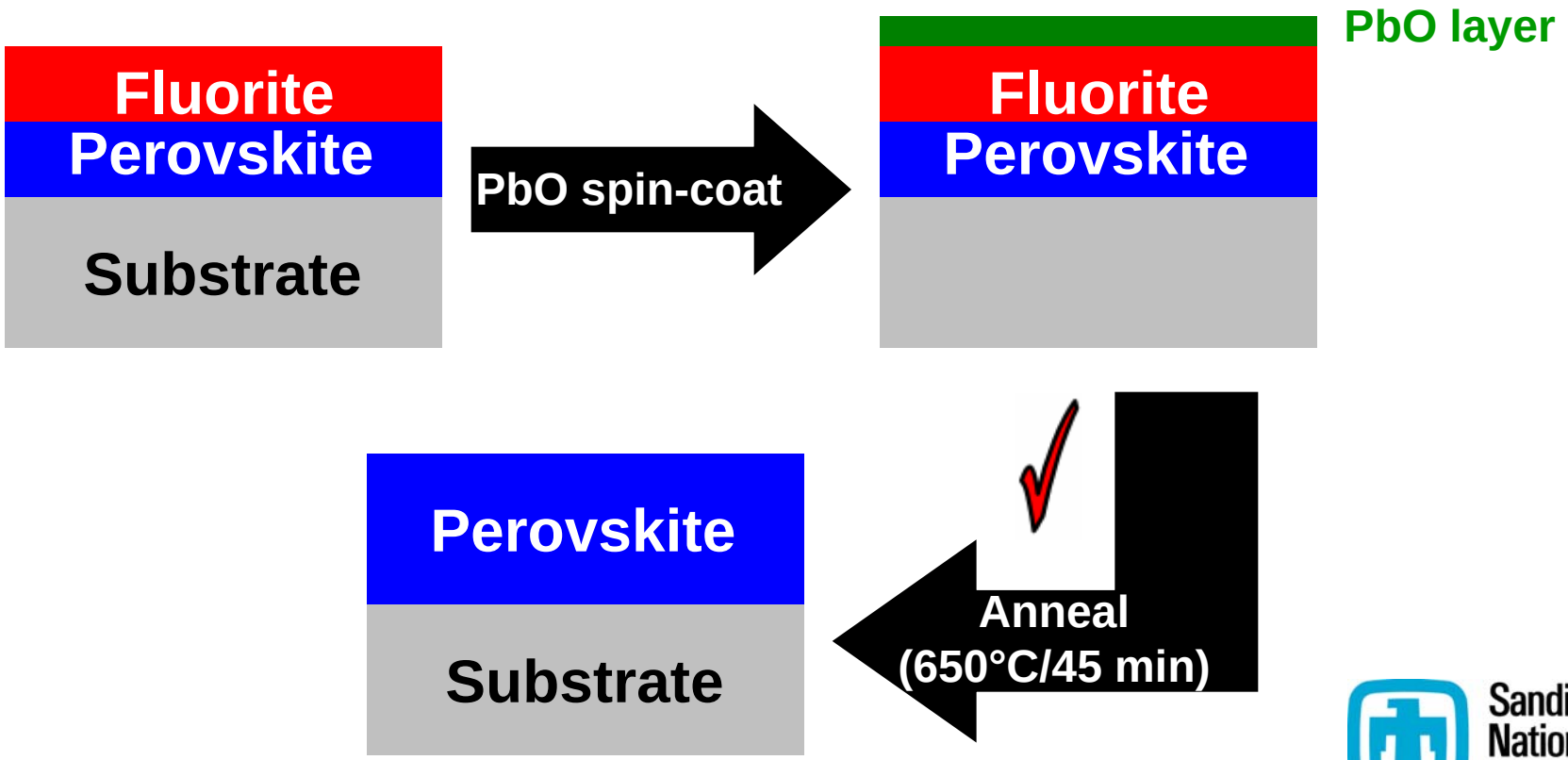


# We have confirmed our hypothesis

***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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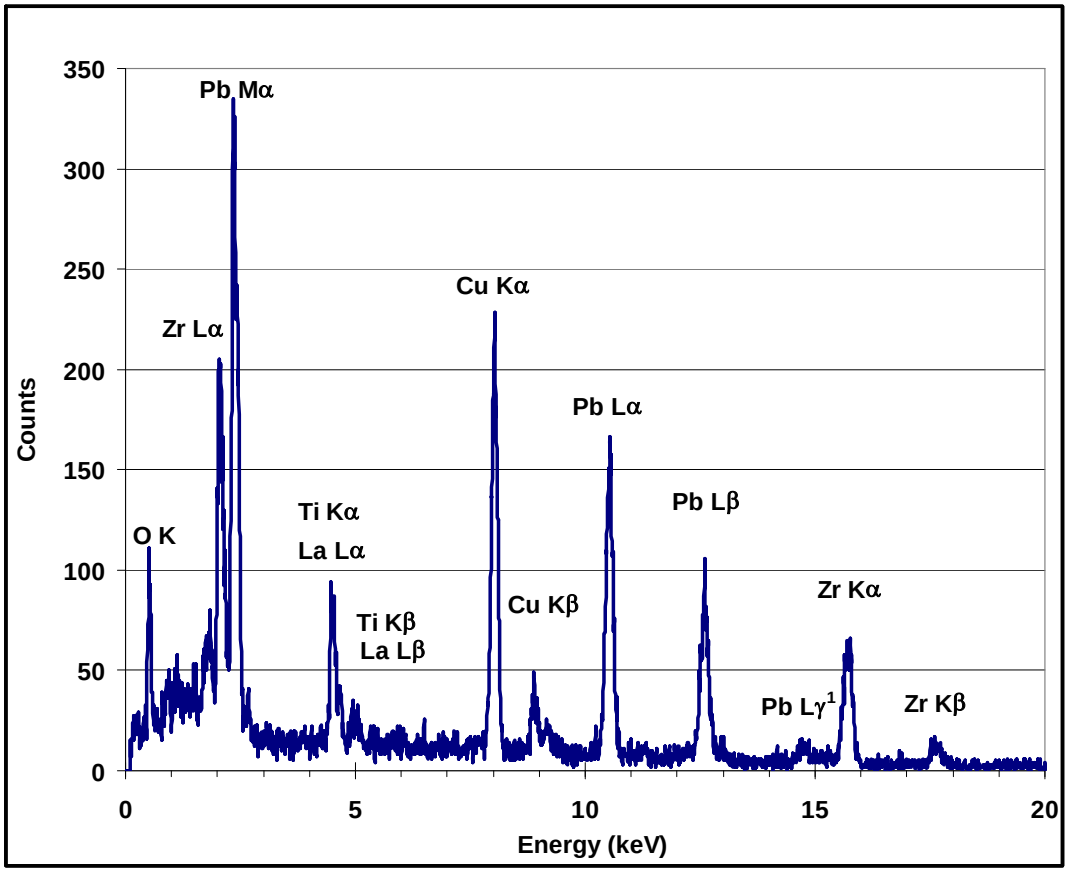
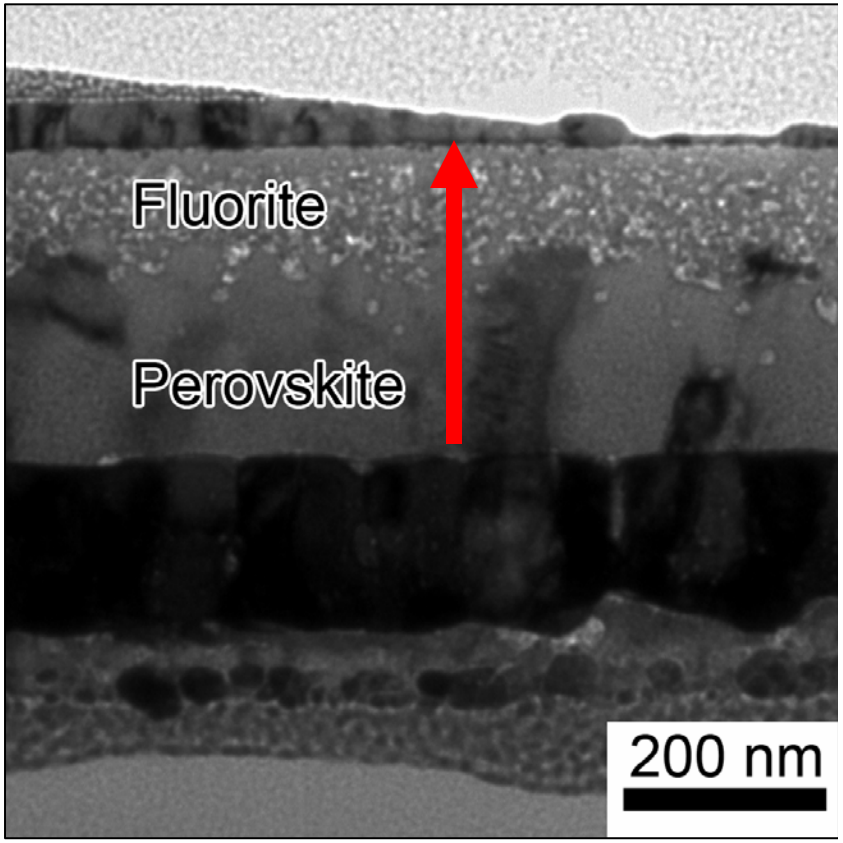
# Can we confirm our proposed mechanism of Pb-replenishment using EDS?

## Typical point spectrum




## EDS linescan direction




**PLZT 12/70/30**



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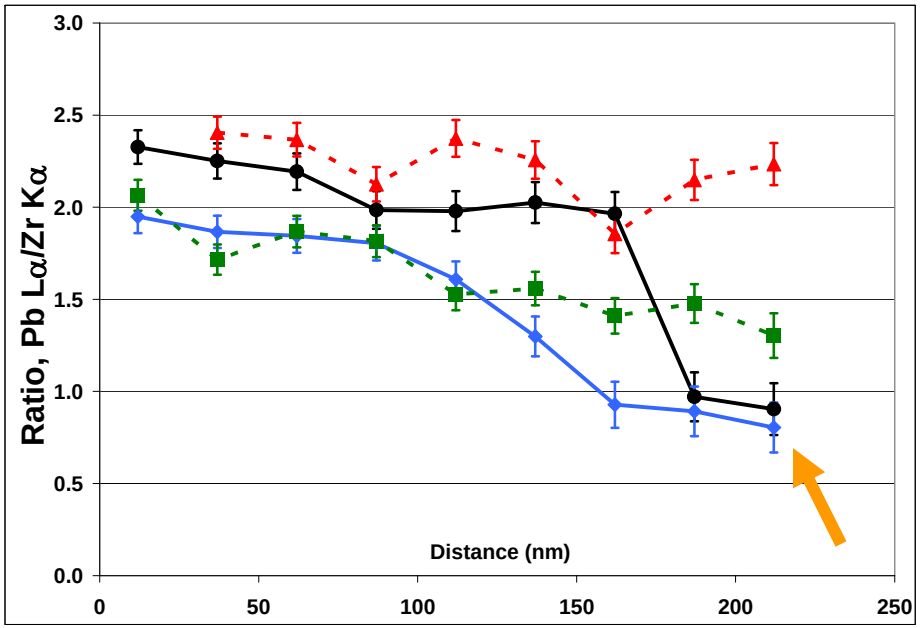
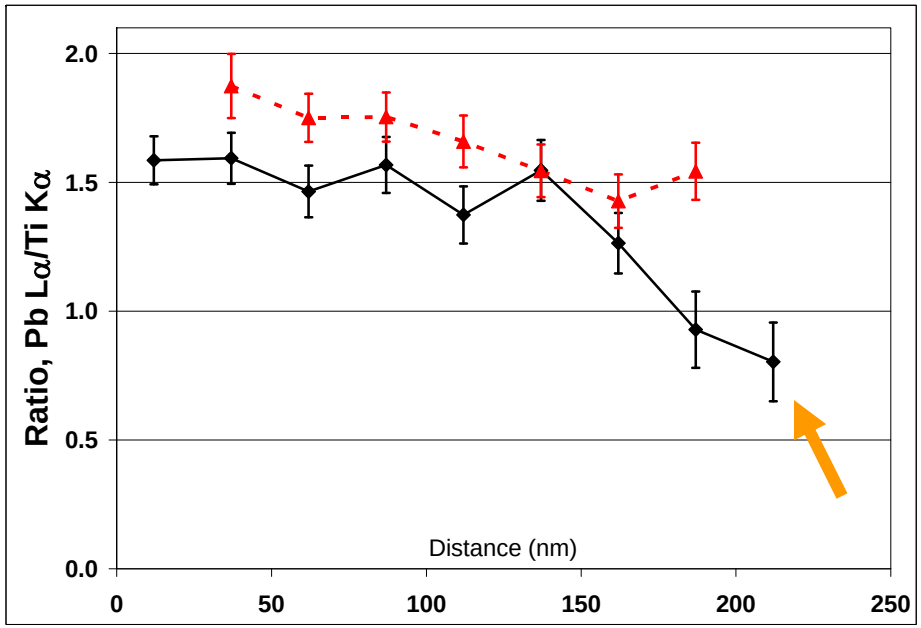
# In the two-phase samples, the Pb content drops significantly near the surface (fluorite)

## Pb to Zr ratios




## Pb to Ti ratios




±3σ

- – – PZT 53/47, single phase
- ——— PZT 53/47, two phase
- – – PLZT 12/70/30, single phase
- ——— PLZT 12/70/30, two phase



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# We have shown that Pb-deficient P(L)ZT can be converted to perovskite after annealing

**This may allow us to use less Pb-excesses to minimize substrate interactions**

**We have confirmed this result with electrical measurements, XRD, and TEM**

**We next hope to perform quantitative TEM-EDS analyses to help optimize the annealing parameters**