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Phase and texture evolution in solution deposited PZT thin films

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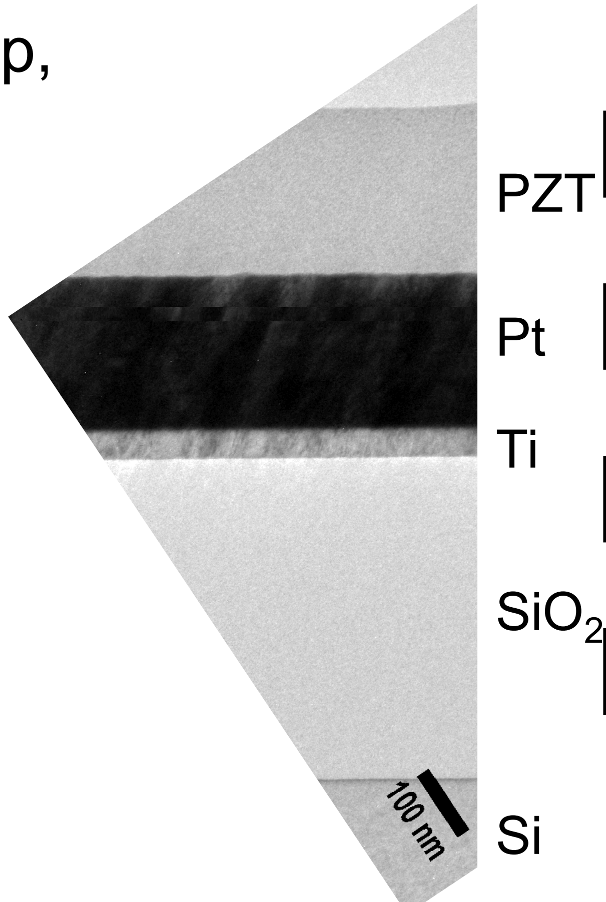
Outline

1. Introduction
   – Motivation
   – Methodology
2. Phase evolution (UF)
   – Effect of Nb doping
   – Pb content in solution
3. Phase and Texture evolution (APS)
   – Effect of heating rate
   – Cation segregation in thin film
4. Ongoing and Future work
5. Conclusions

Solution deposition of PZT films

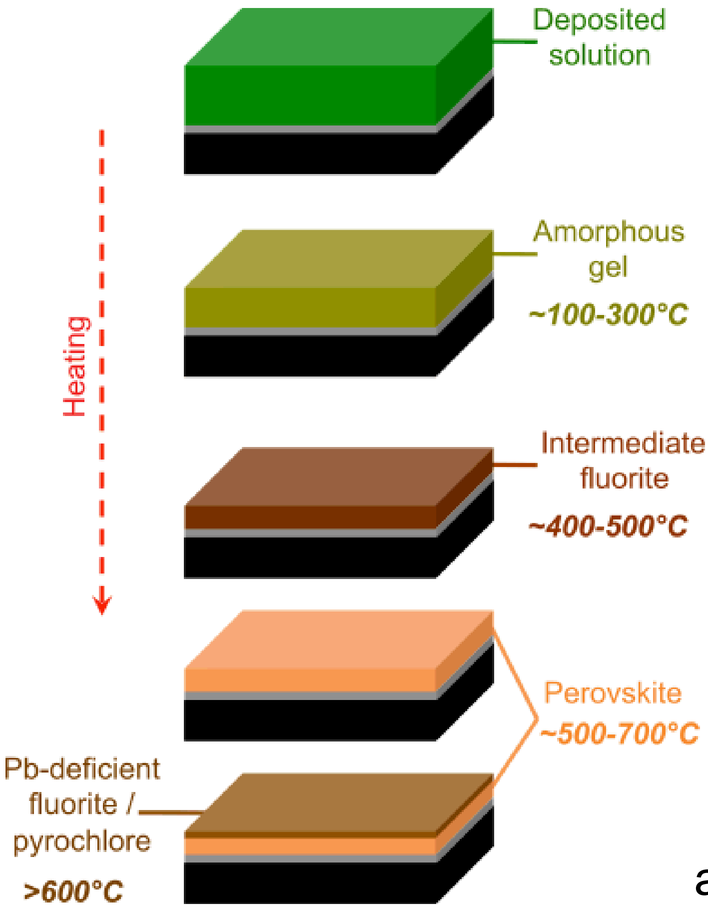
- Solution deposition is cheap, simple, and versatile (deposit on foil, platinized Si, etc.)

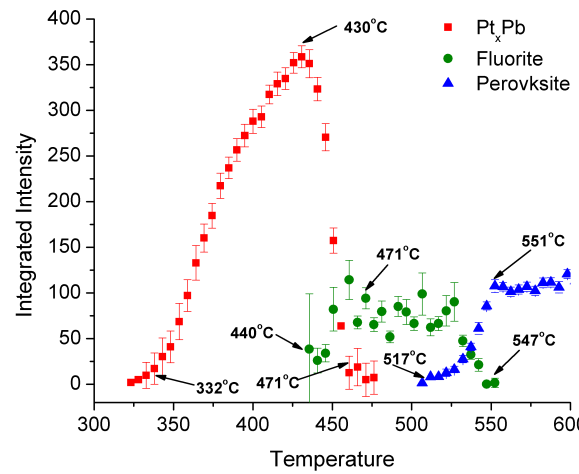
- PZT films are commonly deposited on platinized silicon substrates



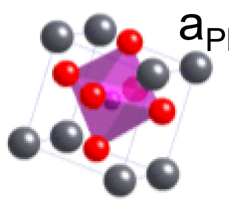
Solution Preparation
↓
Spin Coating
↓
Pyrolysis (300 °C-400 °C)
↓
Crystallization (~700 °C)

Phase evolution during processing



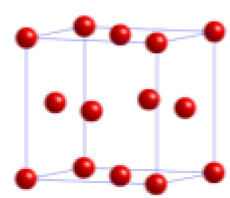


Phase evolution during crystallization[2]



$a_{PbTiO3,\ 500°C}$ = 3.96 A

$a_{Pt,\ 500°C}$ = 3.94 A



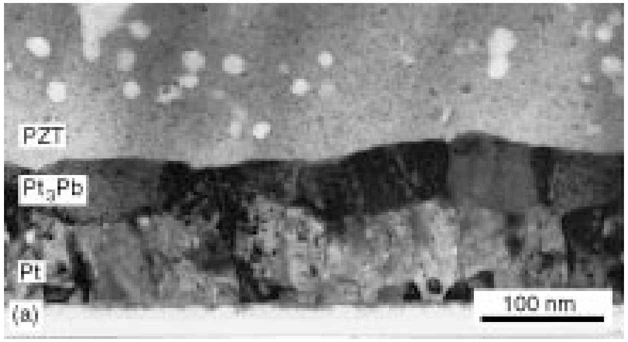
- Ensure complete conversion of fluorite type phase to perovskite phase
- Avoid formation of Pb deficient fluorite type phase
- Minimize reaction between film and the electrode

G. L. Brennecka *et al.* J. Am. Ceram. Soc. 93 (2010) 3935.

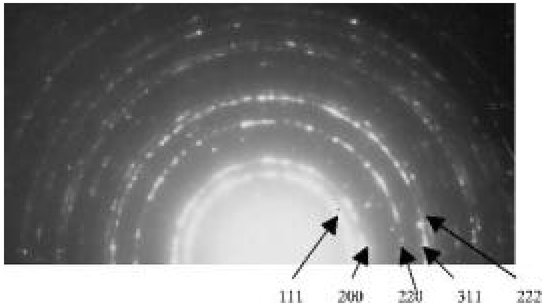
[2]K. Nittala et al, Journal of Materials Science 2011.

Phase evolution: influence on texture

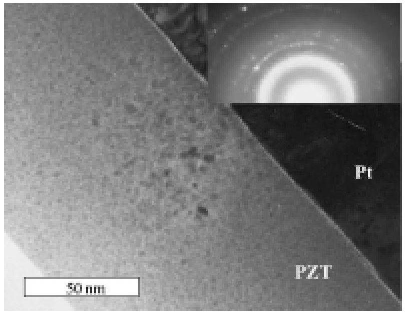
- Heating rate: (111) texture is caused due to nucleation of perovskite on Pt_xPb.[3]
- Fluorite crystallinity: degree of crystallinity controls the final film texture.[4]
- Pt_3Ti [6] and TiO_2 [7] seeds at the film-Pt interface.



Pt_xPb phase forms at the interface of the Pt electrode and the thin film.[5]



Pyrolysis: 350°C, 10s
(111) texture[4]

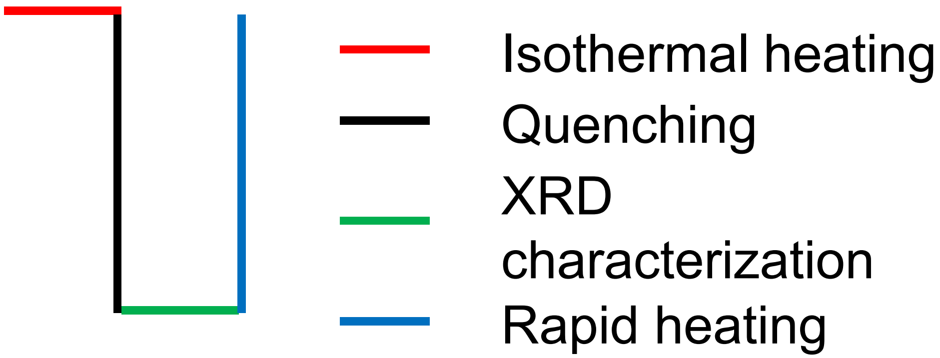


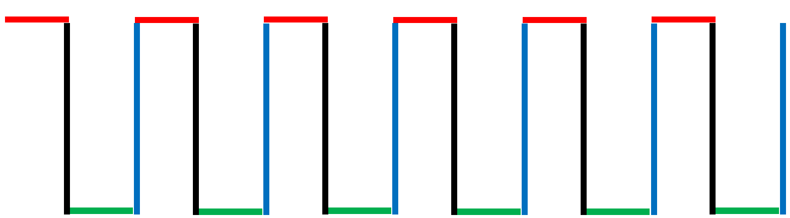
Pyrolysis: 450°C, 2 min
(100) texture

[3]S. Y. Chen and I. W. Chen, J. Am. Ceram. Soc. 81 (1998) 97.
[4]G. J. Norga et al, J. Mater. Res. 18 (2003) 1232.
[5] Z. Huang et al, J. Appl. Phys. 85 (1999) 7355.
[6] T. Tani, PhD Thesis (UIUC, Urbana - Champaign, 1993).
[7] P. Muralt, J. Appl. Phys. 100 (2006) 051605.

Typical approaches for characterization of texture and phase

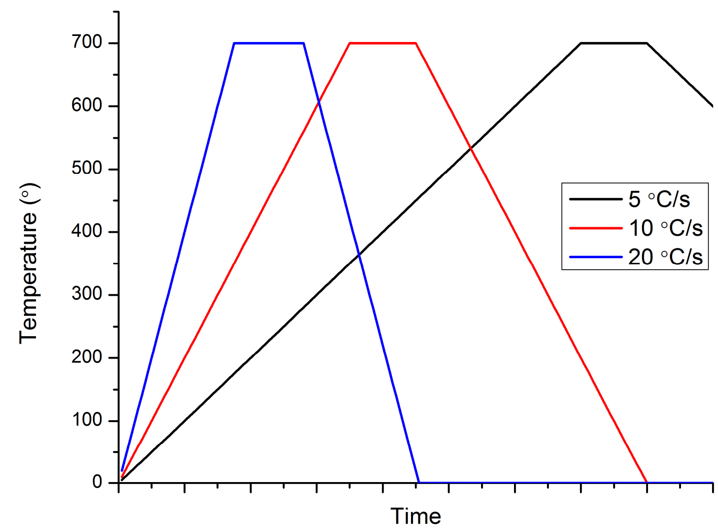
Typical experimental methodologies





Repeated until the thin film completely crystallizes

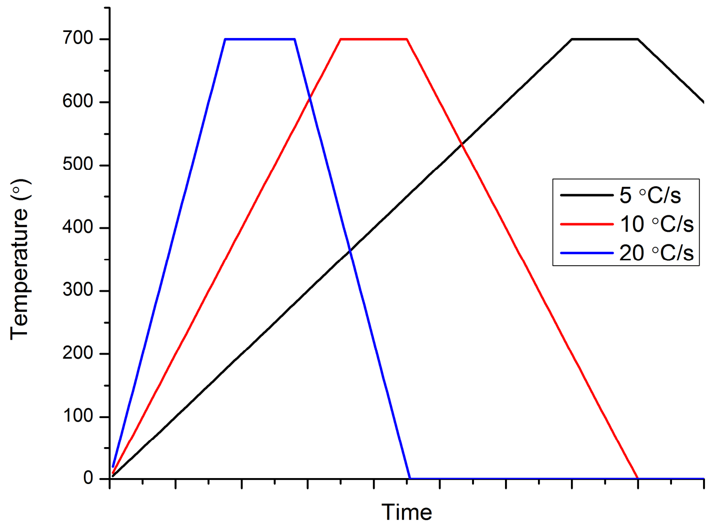
Actual processing conditions



Objective of present investigation

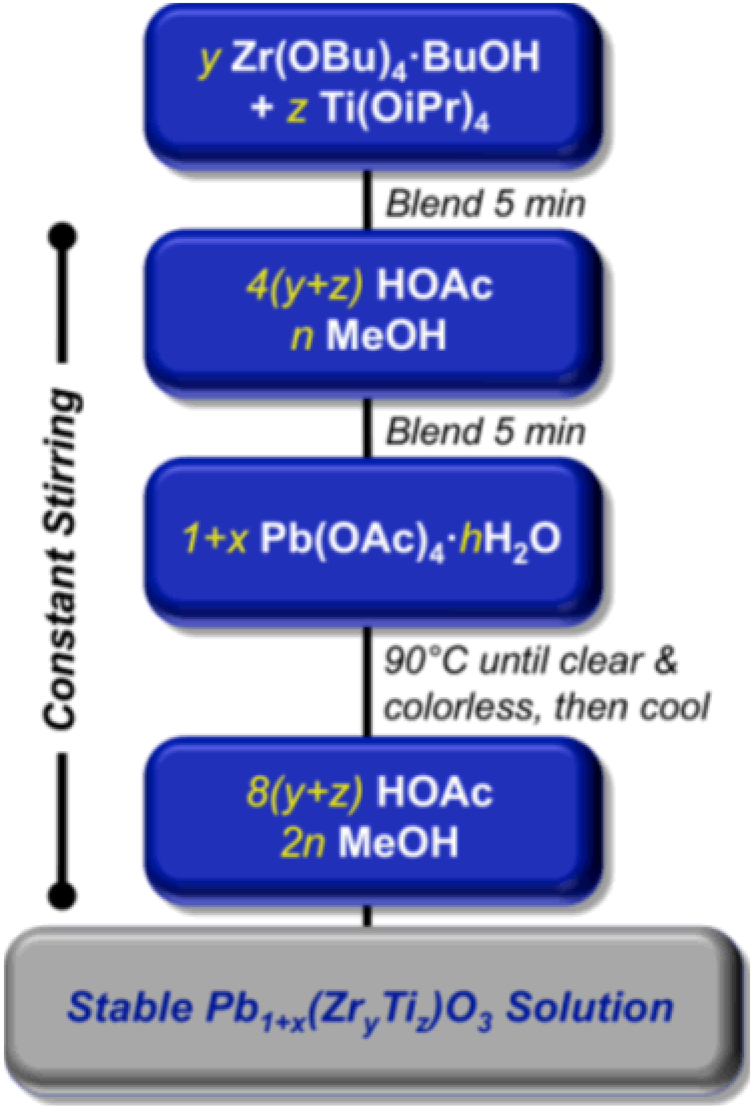
- *in situ* characterization of phase and texture evolution during crystallization to understand the factors affecting final film texture in PZT thin films
- Two different types of *in situ* experiments were performed:
  - Laboratory X-ray (UF)
  - Synchrotron X-ray (APS)

Actual processing conditions



Solution preparation and Film deposition

- Inverted Mixing Order (IMO) process was used for preparation of solutions
- Films deposited on platinized silicon substrates (Pt/Ti/SiO2/Si 170 nm/40nm/300nm/Si)
- Films were spin coated for 30s at 3000 rpm
- Films were pyrolyzed at 300 °C after each deposition step



R. A. Assink and R. W. Schwartz, Chem. Mater. 5 (1993) 511.

G. L. Brennecka *et al.* J. Am. Ceram. Soc. 93 (2010) 3935.

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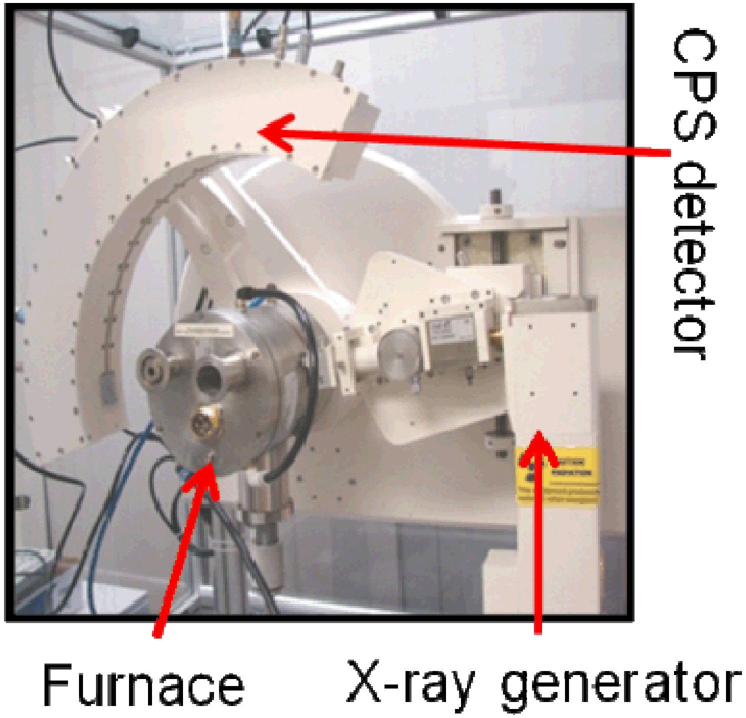
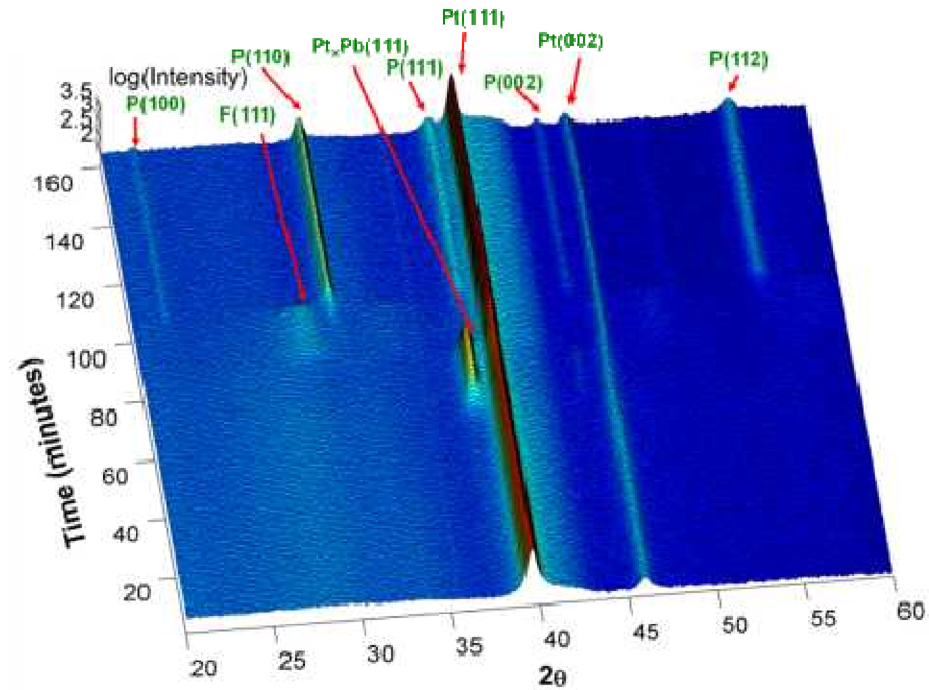
Laboratory XRD





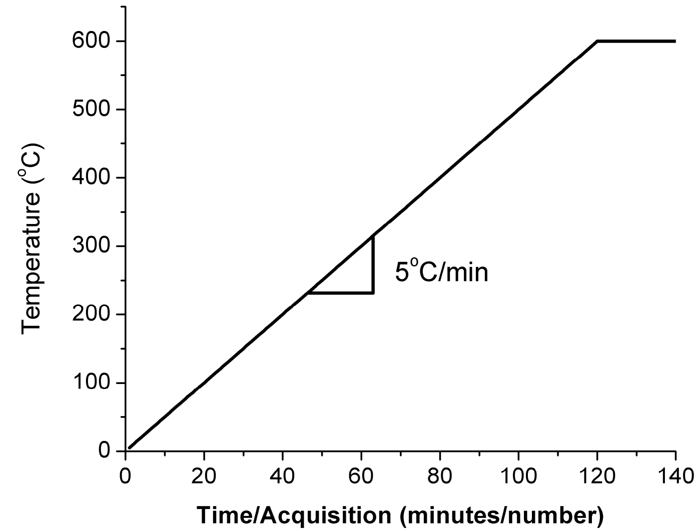
- Inel diffractometer with furnace attachment at UF
- 1-D detector allows for rapid acquisition of diffraction data

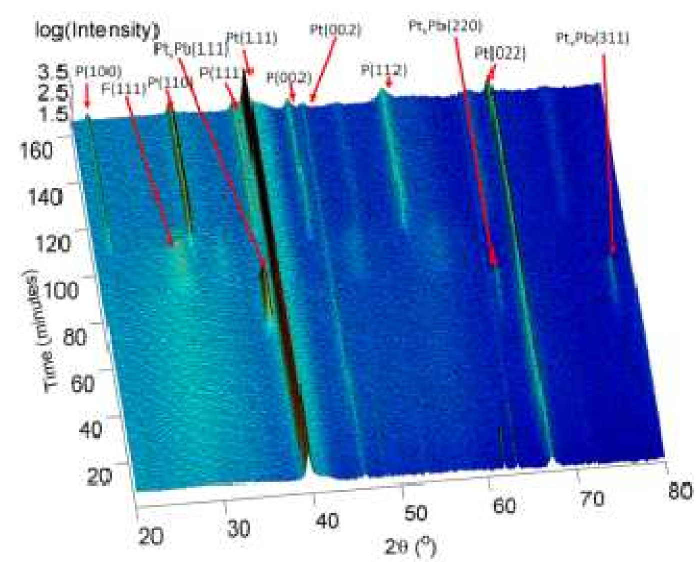
- Diffraction data measured is represented as a contour plot
- Plot shows the evolution of phases during crystallization

Nittala et al., *Journal of Materials Science 2011, 46, 2148-2154.*

Effect of Nb content

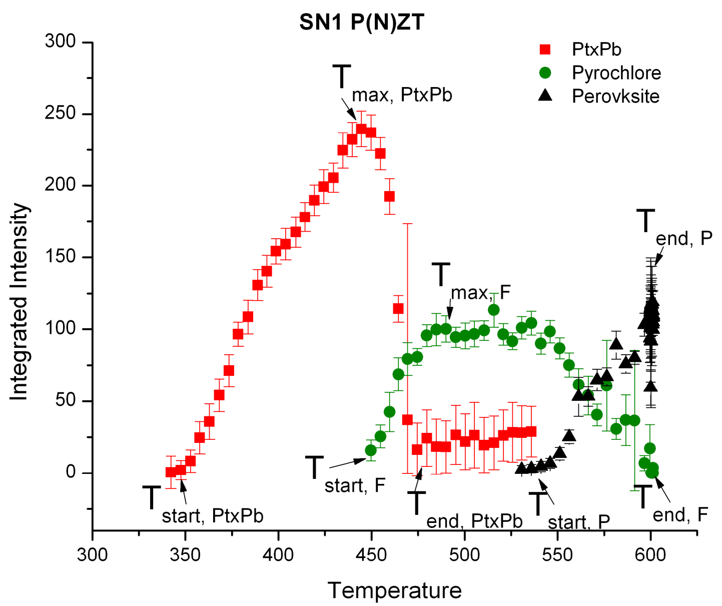
- PZT is routinely doped with Nb and La
- Effect of dopants on phase evolution in solution deposited films is not well understood
- Films were heated 5 °C/min while continuous diffraction patterns were taken





Nb doping: influence on phase evolution

- Temperature at which the Pt_xPb peaks is observed is increased
- Fluorite phase forms ($T_{start,\ F}$) at higher temperature in Nb-doped PNZT compared to undoped PZT thin films
- PNZT: Perovskite formation is complete at 624 °C



	$T_{start,PtxPb}$	$T_{max,PtxPb}$	$T_{end,PtxPb}$	$T_{start,\ F}$	$T_{max,F}$	$T_{end,F}$	$T_{start,P}$	$T_{max,P}$
PNZT 4/52/48	**350.8**	**446.5**	**474.7**	**446.3**	**481.3**	**596.2**	**539.5**	**624.0**
PZT 52/48	**339.4**	**442.0**	**475.1**	**433.5**	**472.1**	**585.5**	**543.3**	**590.4**
Difference	**11**	**4.5**	**~0**	**13**	**9**	**11**	**-4**	**34**

Summary: Nb doping

- Nb doping observed to effect stability of the Pt_xPb metastable phase
- Effect on Fluorite and perovskite formation is consistent with report by Klissurska et al.

R. D. Klissurska,et al., J. Am. Ceram. Soc. 78 (1995) 1513.

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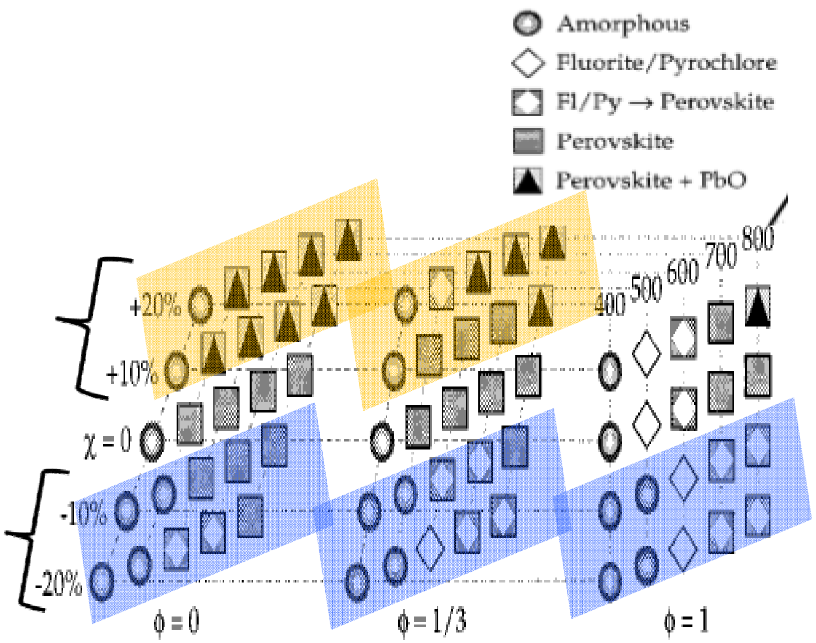
Effect of Pb content on phase evolution

- Pb content was observed to influence phase evolution for solution derived powders
- Presence of substrate introduces additional factors of influence
- Phase evolution of PLZT (6/52/48) 20% Pb films was investigated

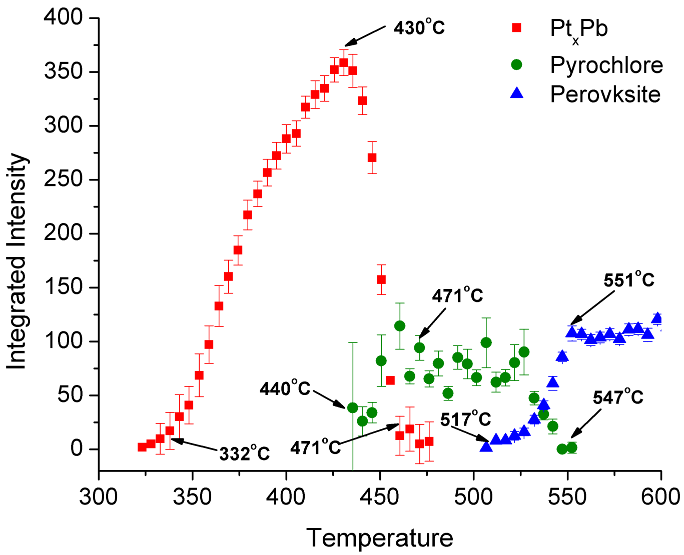


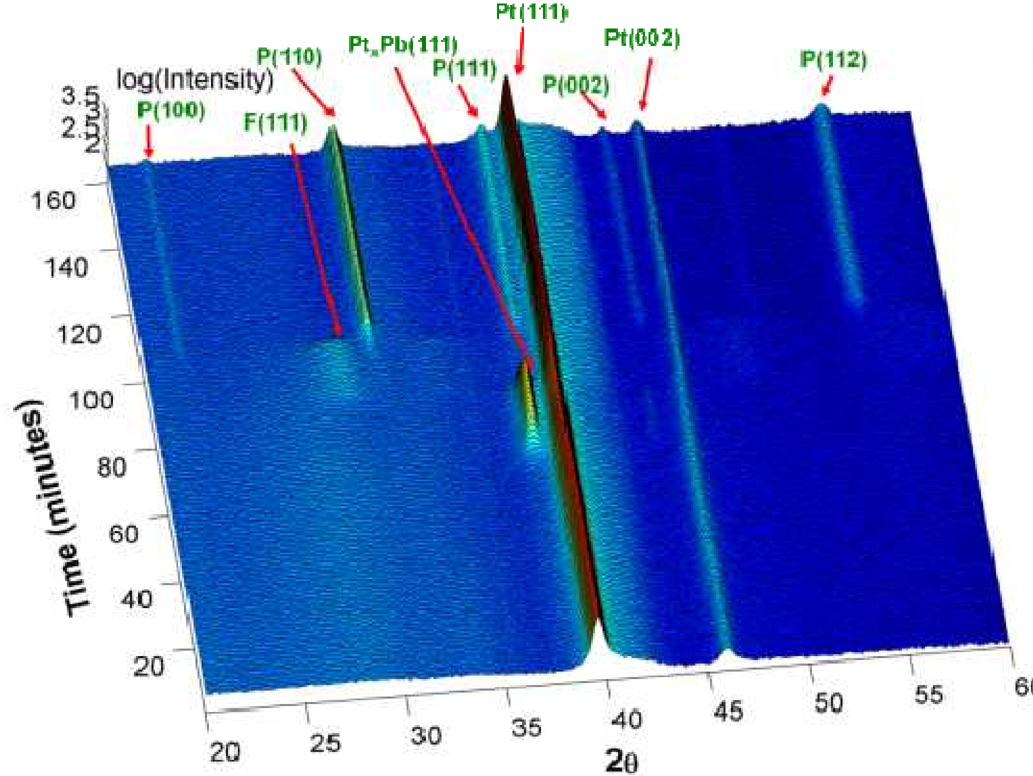
Experimental conditions
Heating rate: 5 C/min
Acquisition time: 60 s

A. D. Polli, F. F. Lange, C. G. Levi, *Journal of the American Ceramic Society* ***2000, 83, 873.***

Phase evolution: Pb excess

- Pt_xPb is the first phase to form
- Fluorite phase (F) is observed as Pt_xPb starts to disappear

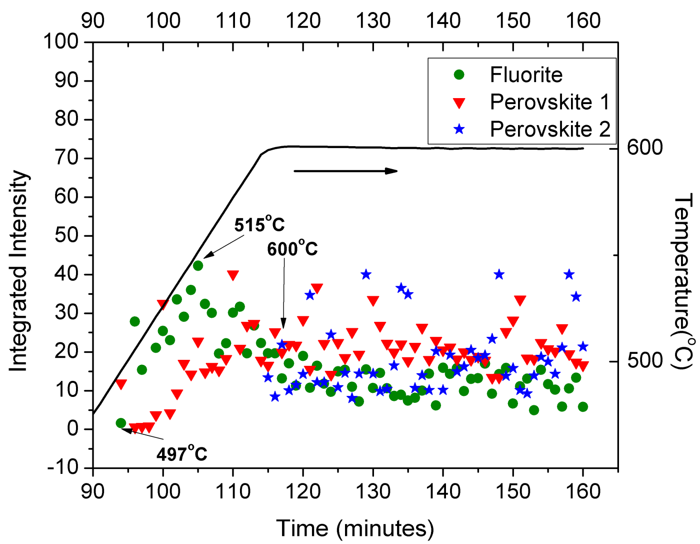


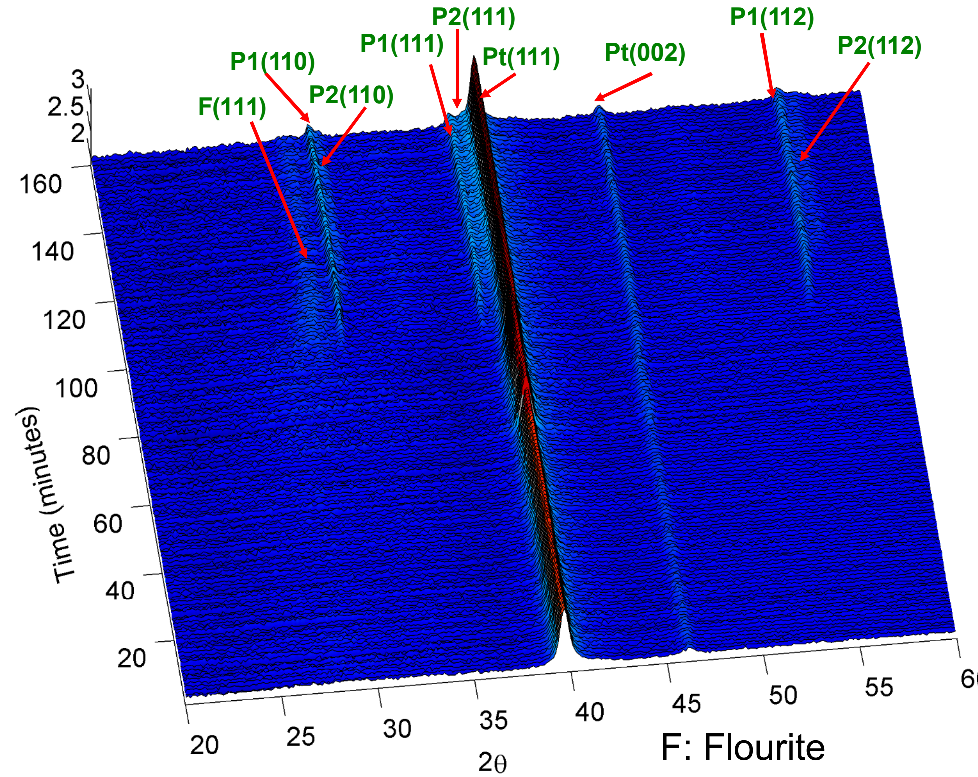


- Fluorite finally disappears and Perovskite (P) appears
- Result agrees with previous studies

Phase evolution: Pb deficient

- Fluorite(F) and Perovskite(P1) phase observed to form together at 515°C
- A secondary perovskite phase(P2) is observed to form on holding at 600°C

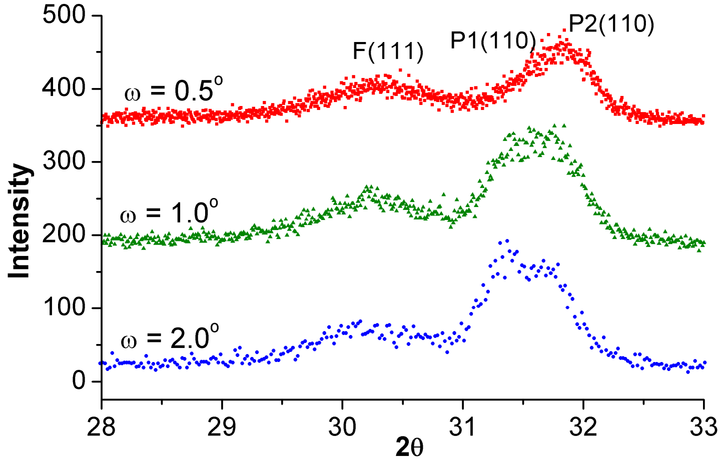




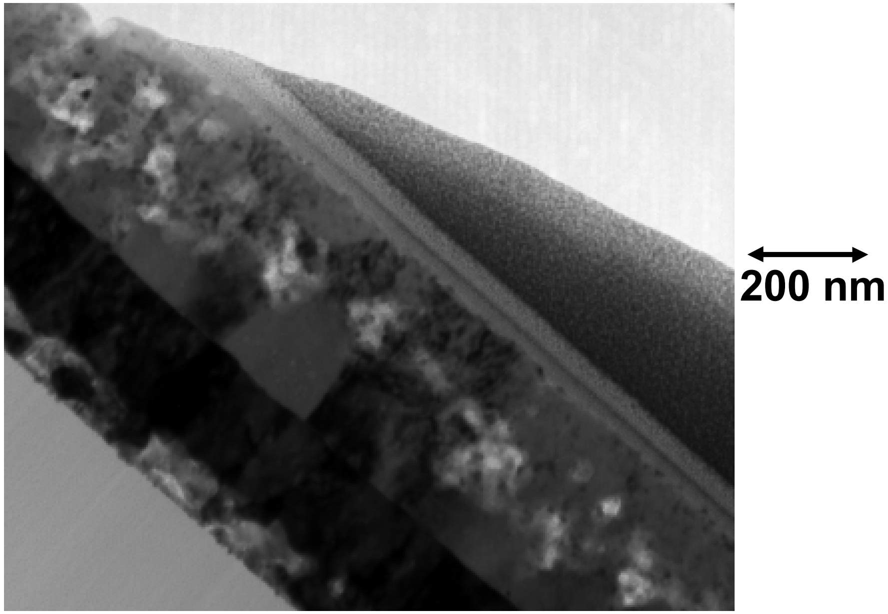
F: Flourite
P1: Perovskite 1
P2: Perovskite 2

Composition	Lattice parameter (Å)
Pb-excess; Perovksite	4.08
Perovskite 1	4.08
Perovskite 2	4.02

Formation of secondary perovskite phase



GIXRD of Pb-deficient film



- Secondary Perovskite could possibly form from Fluorite phase

Summary: Effect of Pb content

- No Pt_xPb was observed in Pb-deficient thin films
- Reaction between the thin film and electrode is reduced
- Temperatures of formation of the fluorite phase is increased for Pb-deficient films
- Perovskite formation is observed at the same temperature for both Pb-excess and Pb-deficient films

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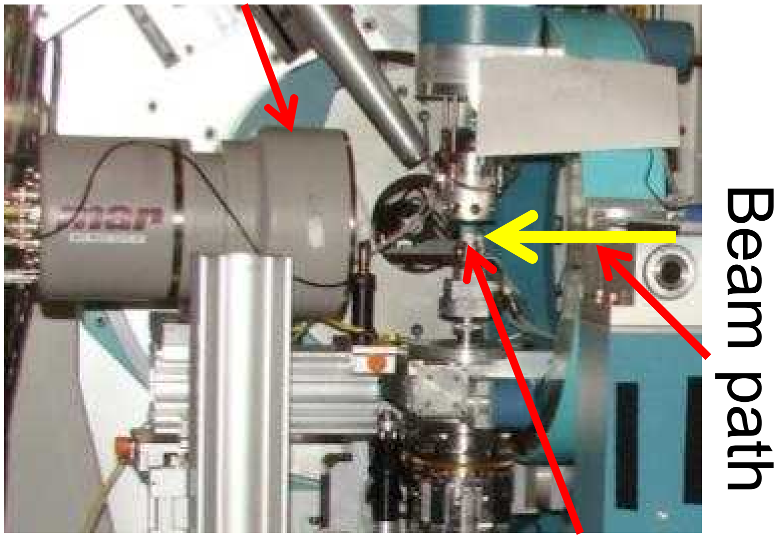
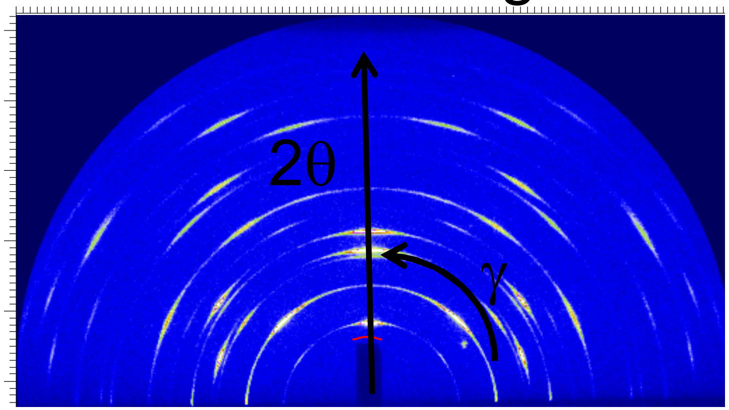
Setup at APS

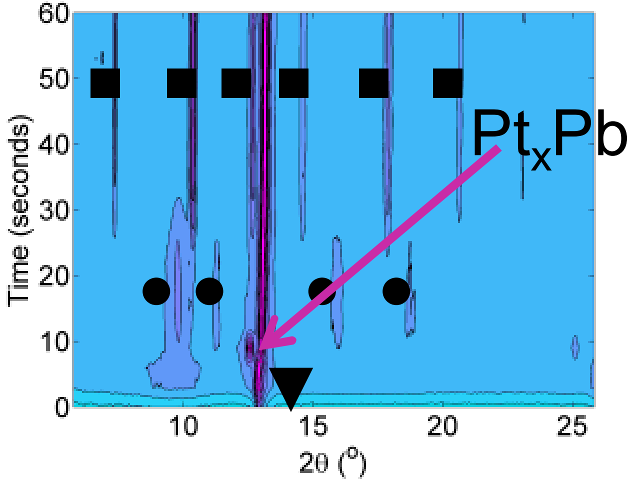
2D - detector



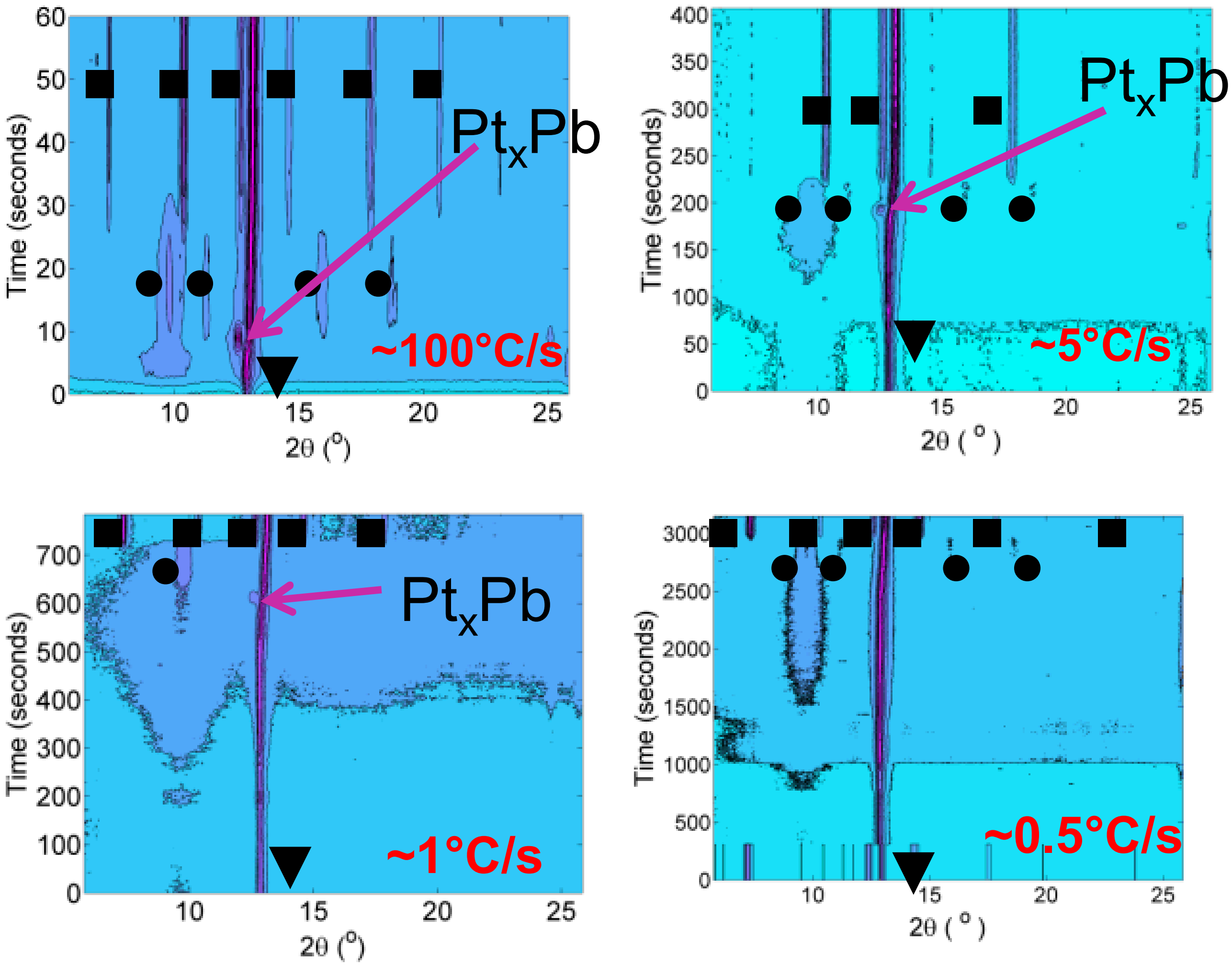
- Synchrotron X-ray source (APS)
- Heating rates: ~100 °C/s to 1°C/s
- 2-D detector captures texture and phase information
- 1s acquisition time, continuous acquisition

Diffraction angles





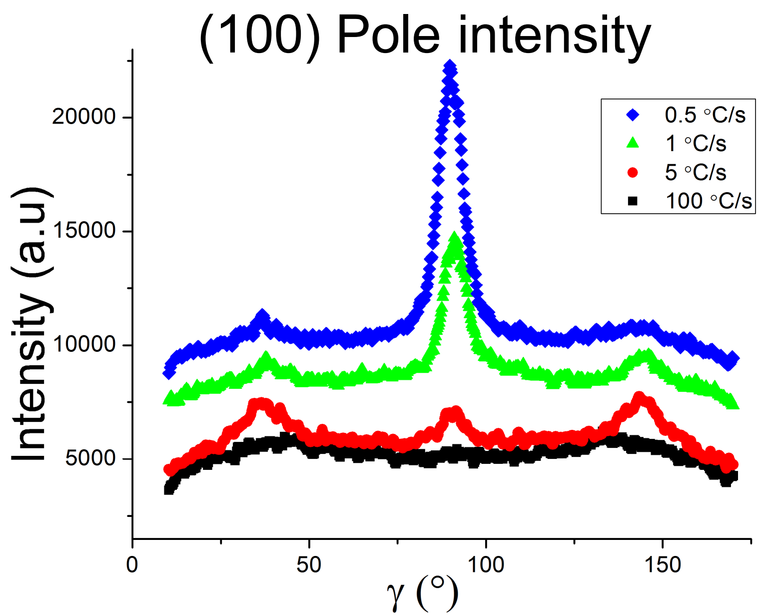
Heating rate influences phase evolution

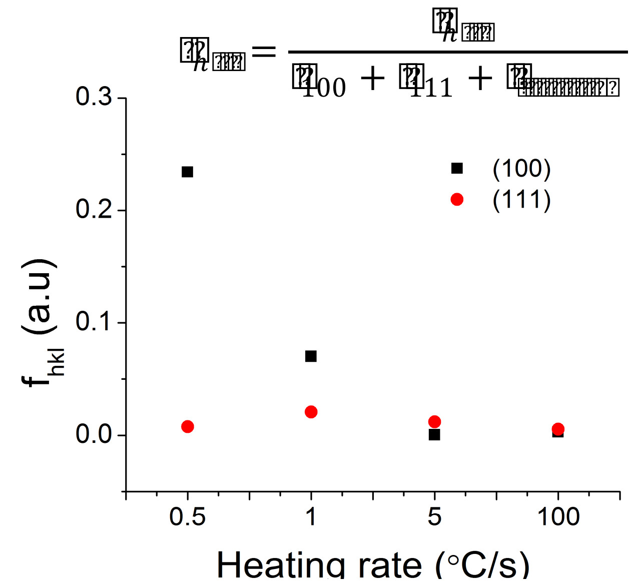


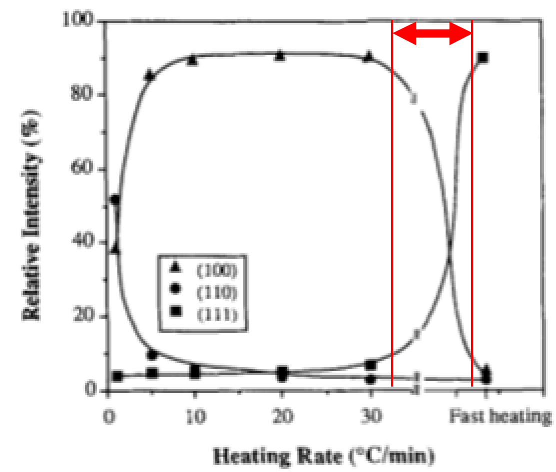
- Sequence of phase evolution: (1)Pt$_x$Pb, (2)Fluorite, (3)Perovskite
- No overlap in Pt$_x$Pb and perovskite phases
- Amount of Pt$_x$Pb formed decreases with decreasing heating rate
- Crystallinity of fluorite phase changes with heating rate

▼ Pt ■ Perovskite ● Fluorite

Variation of texture with heating rate





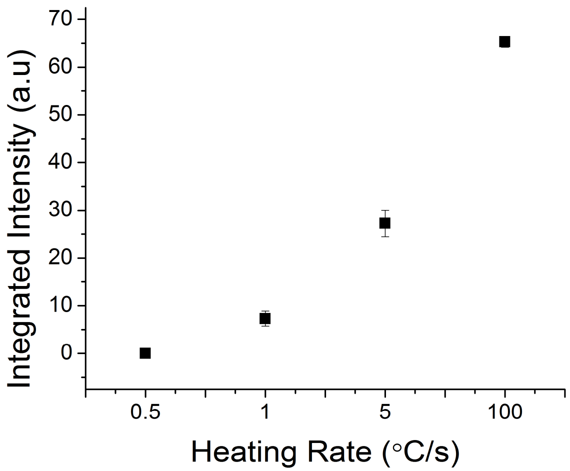


- (100) texture decreases with increasing heating rate
- In fast heating rates, homogenous nucleation may dominate over heterogeneous nucleation

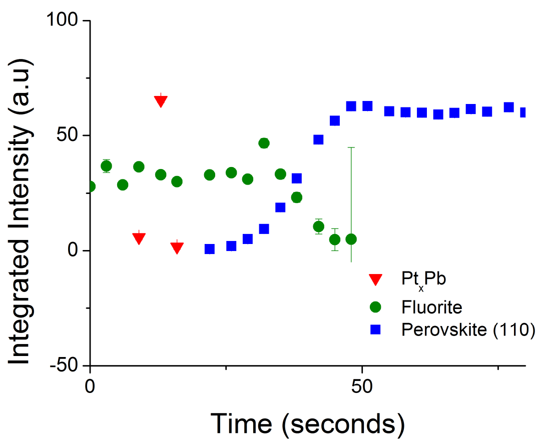
*S. Y. Chen and I. W. Chen, J. Am. Ceram. Soc. 81 (1998) 97.

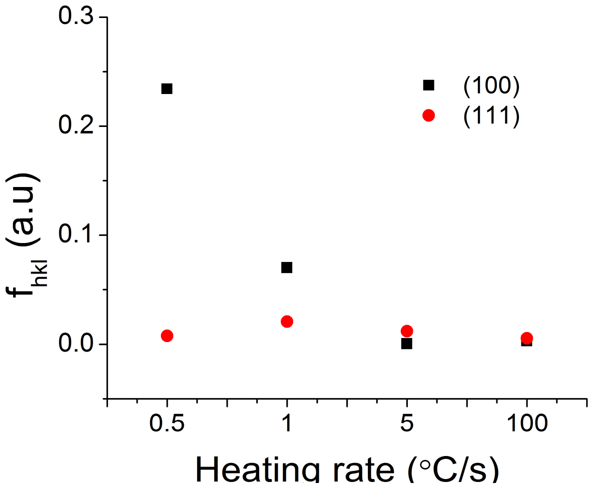
Pt_xPb might not seed (111) texture

- Maximum intensity of Pt_xPb increases with heating rate
- Observed stability of Pt_xPb is consistent with *ex situ* observations*
- No overlap is observed between the Pt_xPb and perovskite
- Weak (111) or random texture obtained for samples with intense Pt_xPb formation



Phase evolution for 100°C/s

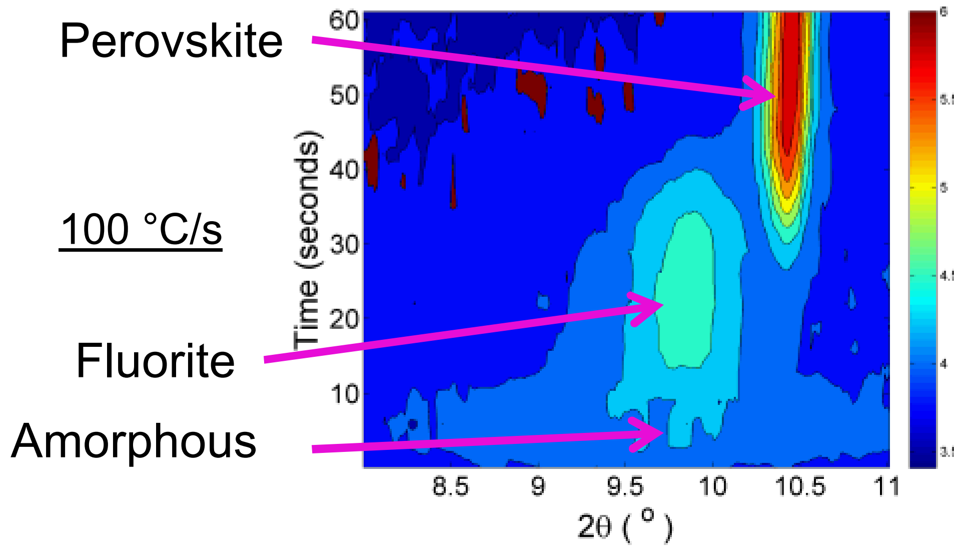




*S. Y. Chen and I. W. Chen, J. Am. Ceram. Soc. 77 (1994) 2332.

Fluorite: evolution and texture

- During crystallization, the fluorite phase is observed to always precede the perovskite phase
- The broad peak characteristic of the amorphous phase continuously transforms into the (111) - fluorite peak
- Trend is observed to be consistent for all the heating rates investigated
- No preferred orientation was observed in the fluorite phase



- Fluorite phase may not seed the (111) orientation in these films

Summary: Phase and texture evolution

- The observed phase evolution sequence is: 1. Pt_xPb, 2. fluorite, and 3. perovskite
- No evidence for seeding of texture by Pt_xPb or fluorite phase is observed

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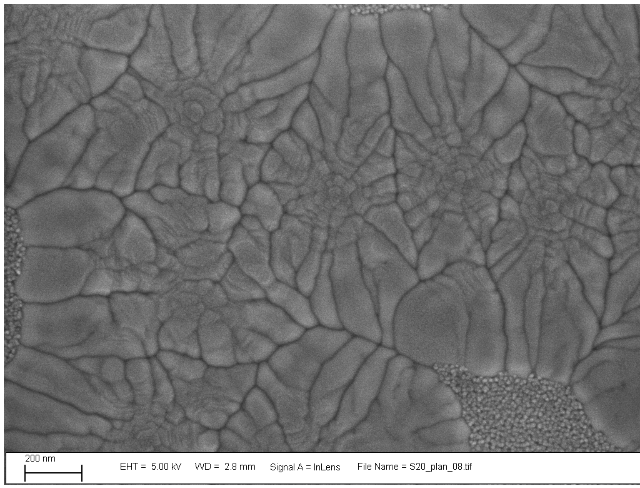
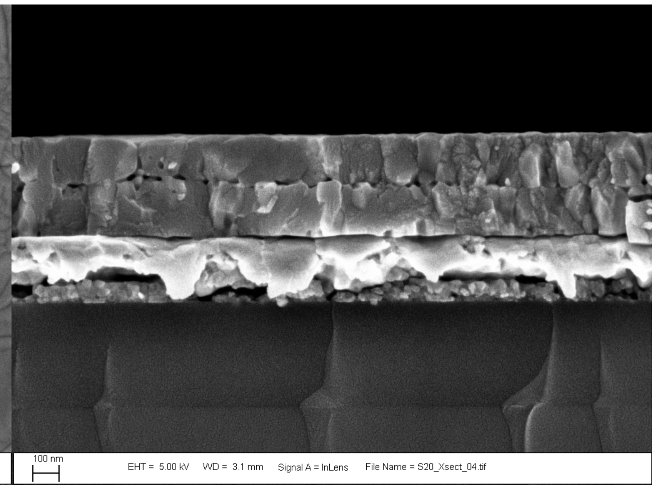
Microstructural characterization

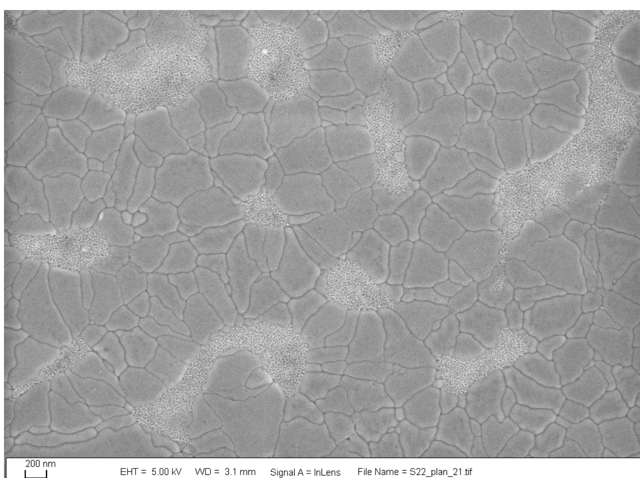


~100°C/s

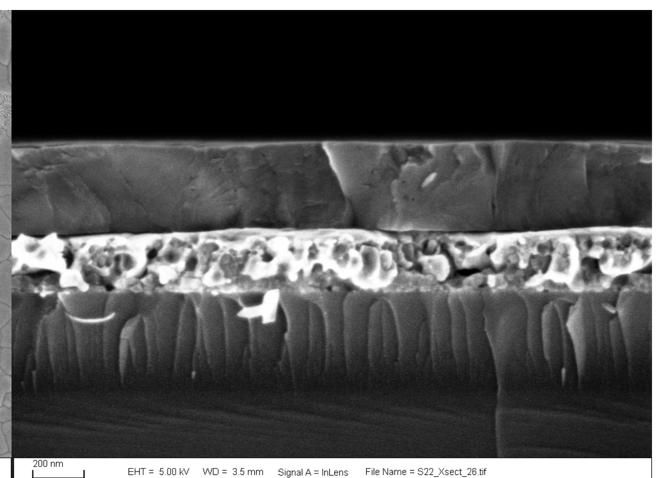


~100°C/s

- Rosette type grain structure in 100 °C/s
- Film crystallized in two layers
- Porosity observed in the middle
- Homogenous nucleation



~0.5°C/s



~0.5°C/s

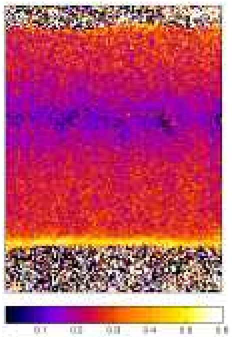
- Columnar type grains observed for 5 °C/s, 1°C/s and 0.5 °C/s
- Nucleation at the film – electrode interface
- Grain size observed to increase with decreasing heating rate

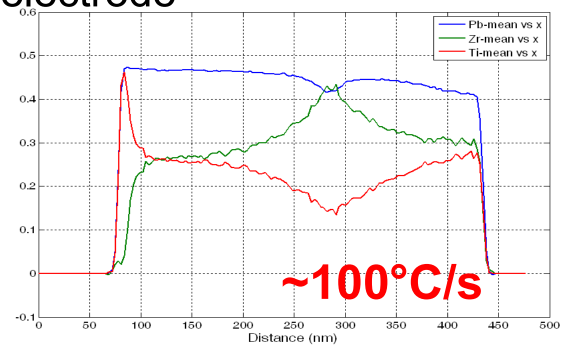
Chemical mapping along thickness

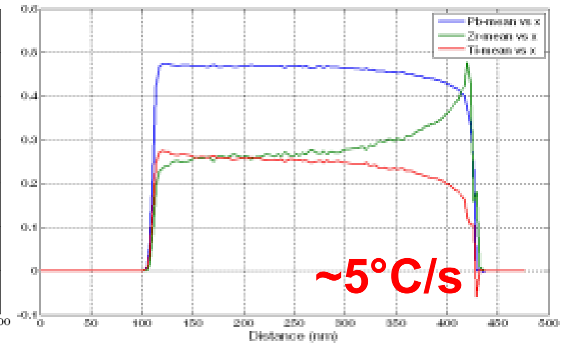
Ti cation maps

Pt electrode | air

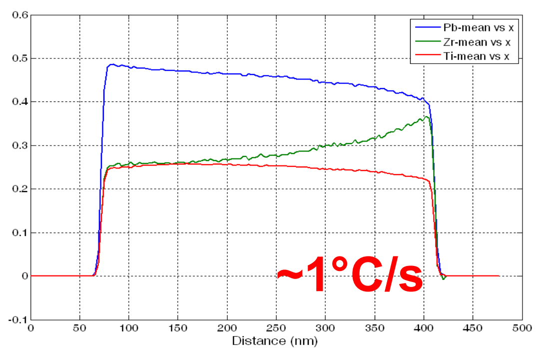
Pt electrode | air

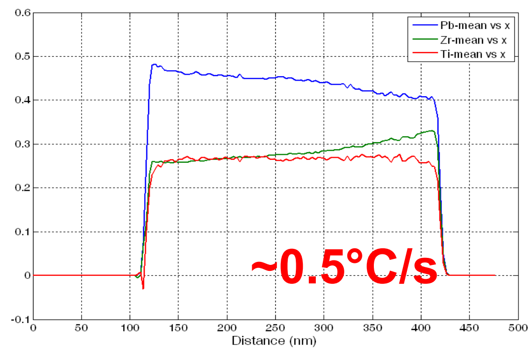






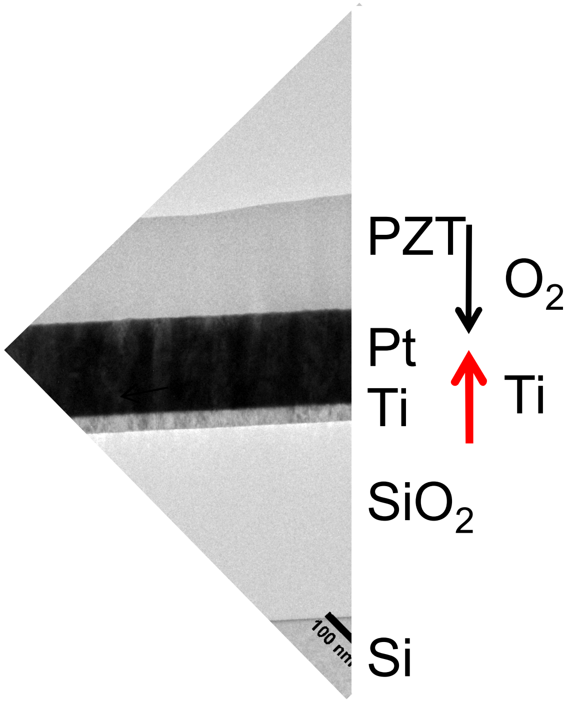
- Preferential Ti segregation near interface
- Zr/Ti segregation through thickness

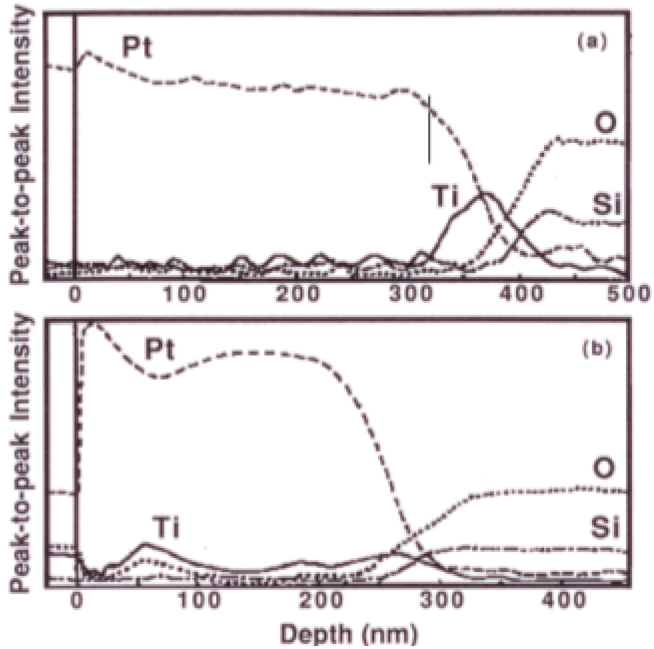




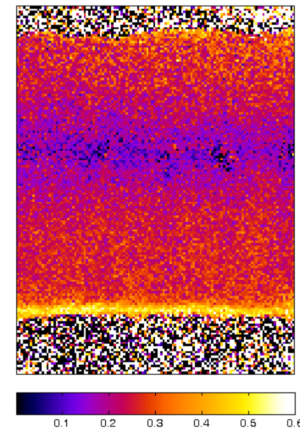
- No preferential Ti near interface
- Some Zr/Ti segregation through thickness, but less than faster ramp rates.

Ti segregation at interface: influence of kinetics





100°C/s



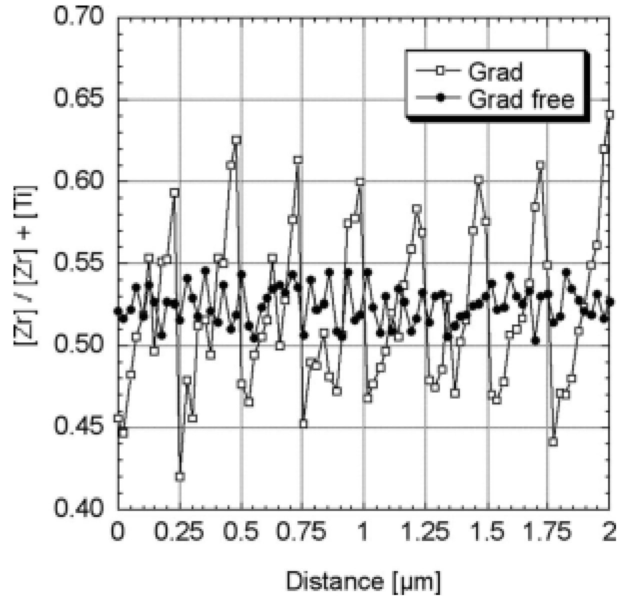
1°C/s

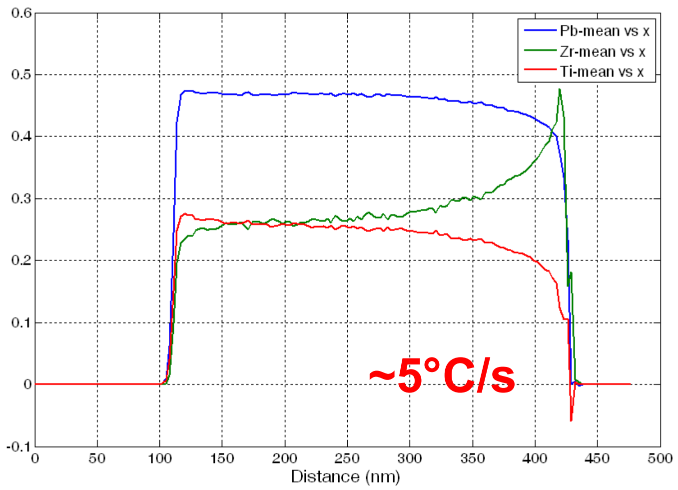
- Pt allows for diffusion of both Oxygen and Titanium
- Diffusion of Titanium species decreases with oxidation
- Considerable Oxygen deficiency in the film allows for diffusion of Titanium to the top of the Platinum electrode

Toshi Tani PhD thesis, UIUC 1992

Zr/Ti variation across thickness of film

- Calame and Muralt reported Zr/Ti segregation across the thickness of the film due to preferential nucleation of Ti-rich composition
- Zr/Ti segregation similar to that observed for in this study
- Intense Ti segregation observed in this study is not reported
- Could be limited by resolution of the probing technique





F. Calame and P. Muralt, Applied Physics Letters 90 (2007).

Conclusions: Cation segregation

- Intense Ti segregation is observed at the thin film – electrode interface for fast heating rates
- Zr/Ti segregation is observed to decrease with decrease in heating rate
- Ti segregation could be due to preferential nucleation of Ti-rich composition or diffusion of Ti from the adhesion layer

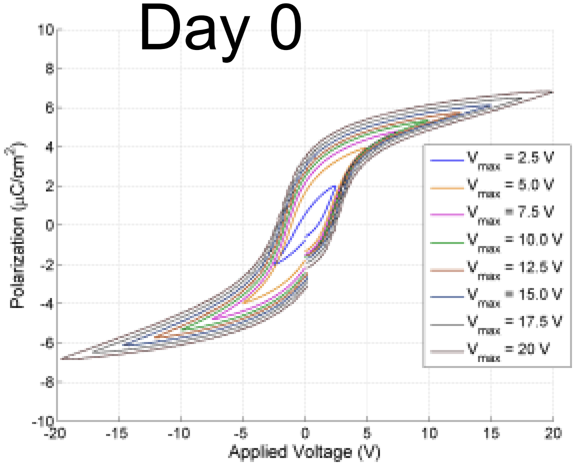
Ongoing and Future work

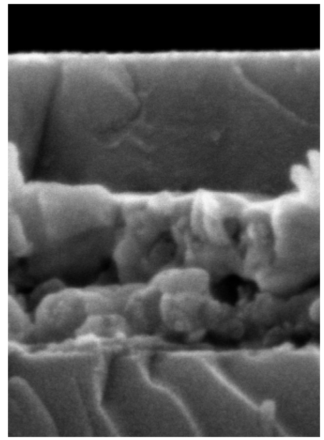
The effect of the following factors on phase and texture evolution is being investigated

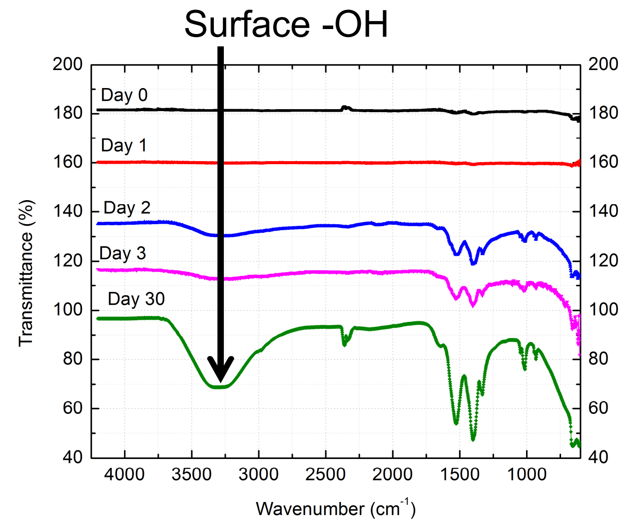
- Adhesion layer
- Solution chemistry (IMO vs Sol-gel)
- Aging in the gel state
- Heating geometry

Aging of pre-crystallized thin films

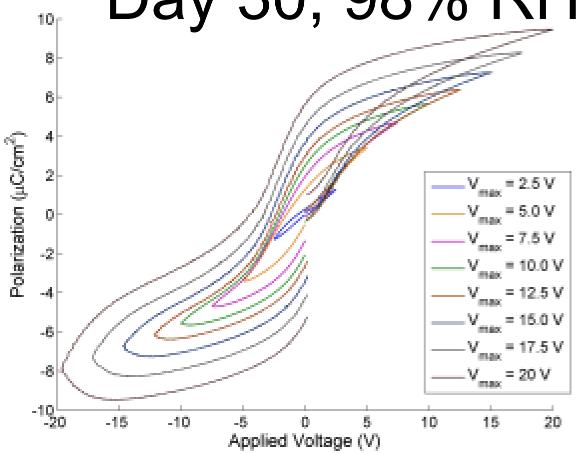
Day 0

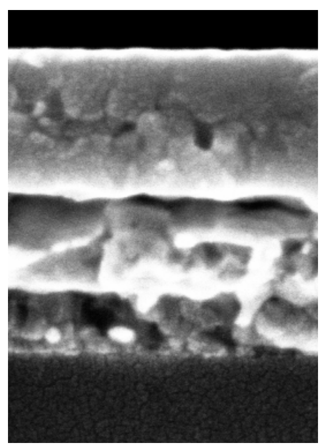


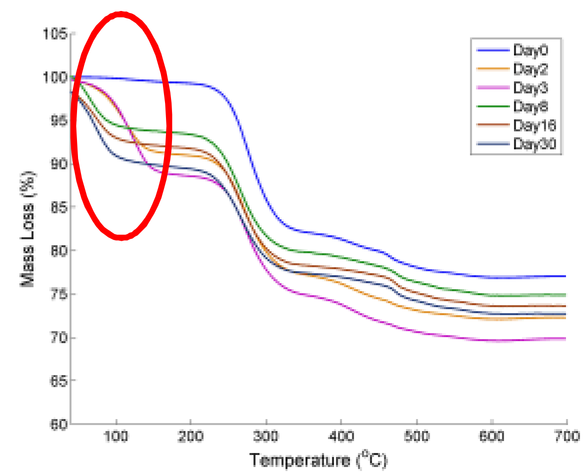




Day 30, 98% RH







Degradation of electrical properties is observed for films aged in high RH conditions

Conclusions

- Nb doping influences the stability of PtxPb, fluorite and perovskite phases
- Pb deficiency in the starting solution leads to decreased reaction between film and electrode
- No evidence for seeding of orientation of the PZT phase by the intermediate phases was observed
- Ti segregation was observed to be more intense for faster heating rates

Phase and texture evolution in solution deposited PZT thin films

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Sungwook Mhin and Katherine Dunnigan

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