SAND2011-3345C

# Phase and texture evolution in solution deposited PZT thin films during slow and fast heating rates


*Nittala*

Jacob L. Jones[1], Krishna Nittala[1],
Geoff L. Brennecka[2], Jon F. Ihlefeld[2], Bruce A. Tuttle[2], and
Douglas S. Robinson[3]

[1]*Department of Materials Science and Engineering, University of Florida, Gainesville, FL, USA*
[2]*Sandia National Laboratories, Albuquerque, NM, USA*
[3]*Advanced Photon Source, Argonne National Laboratory, Argonne, IL, USA*

1 UF UNIVERSITY of FLORIDA College of Engineering
2 Sandia National Laboratories
3 Argonne NATIONAL LABORATORY

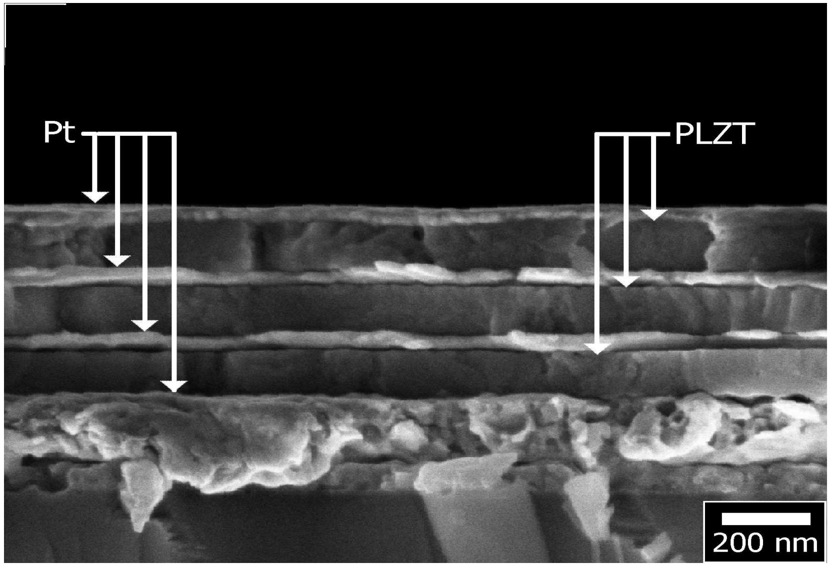
***Support***: *Supported by the National Institute for NanoEngineering (NINE) and the Laboratory Directed Research and Development (LDRD) program at Sandia National Laboratories. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.*

# Outline

1. Introduction
   – What we already know about processing, texture, characterization, etc.
   – Objective of present investigation (*in situ* crystallization)
2. Experimental Technique 1:
   – Laboratory X-ray Diffraction of PLZT±20%Pb
3. Experimental Technique 2:
   – X-ray Diffraction using Synchrotron of PZT±10%Pb
4. Conclusions

# Background

- Lead zirconate titanate (PZT) based thin films are used in many applications including high power capacitors
- Multilayer stacks can provide much higher energy density per unit area.
- Platinum used for bottom electrode material
  - good electrical conductivity
  - oxidation resistance



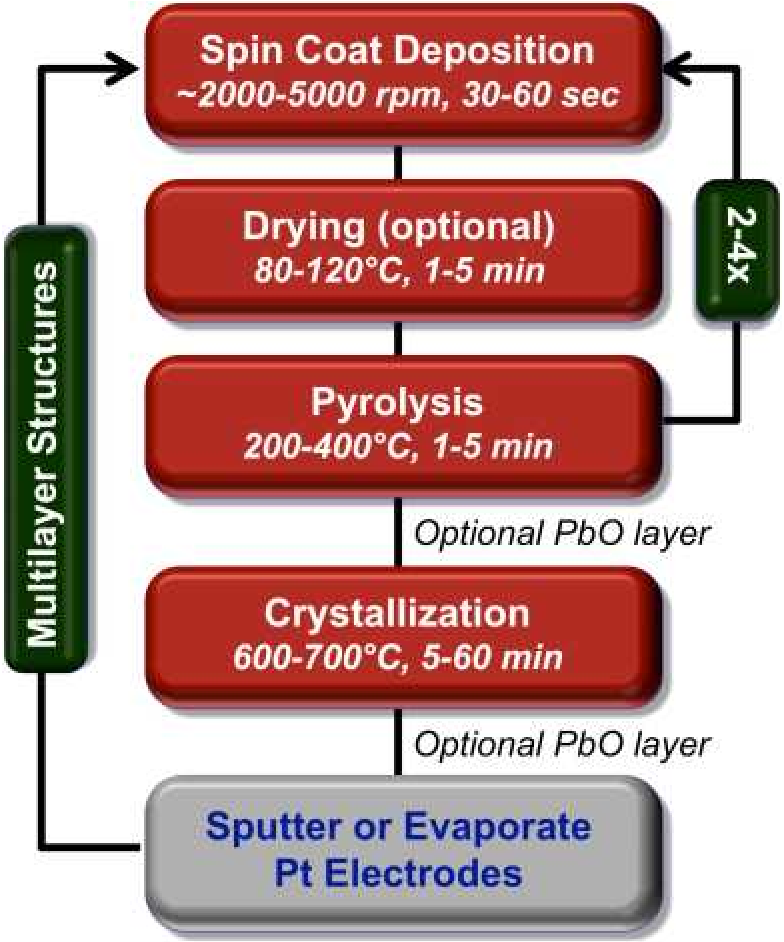

Multilayer stack of PLZT thin films with film thickness of ~ 120 nm.

- As devices become smaller, interface (Pt-PZT) effects dominant

G. L. Brennecka et al., *Journal of Materials Research 2008, 23, 176.*

# Processing: Deposition

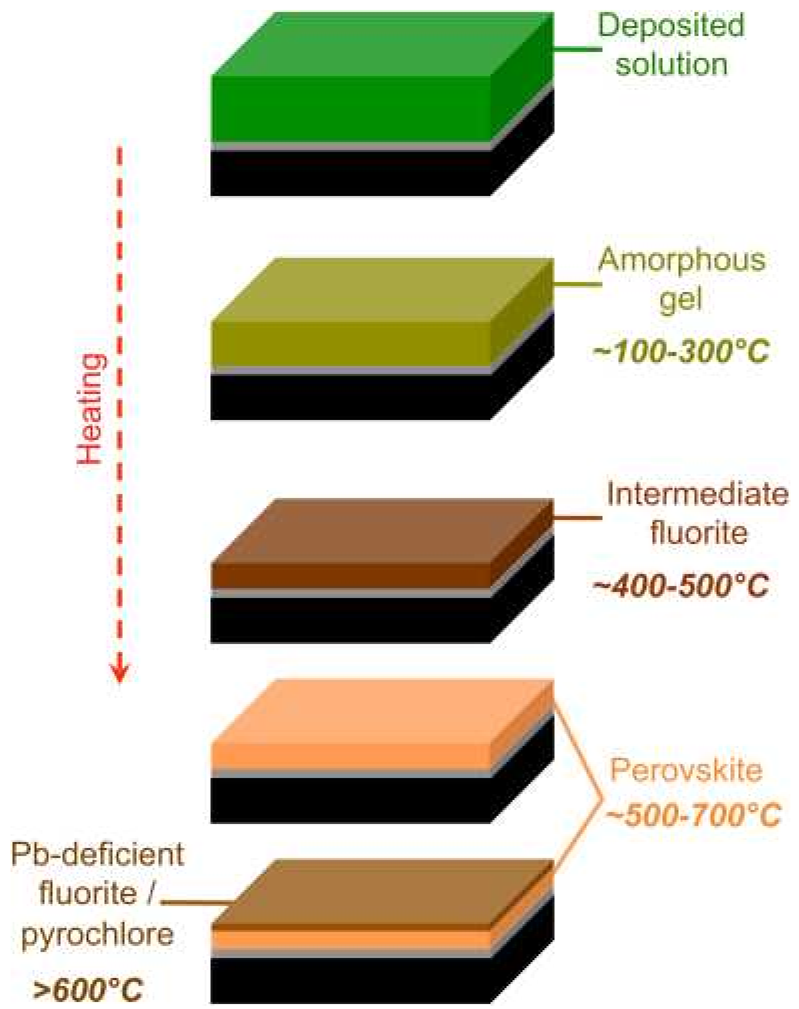
- Solutions with required final cation ratios are prepared
- Solutions are spin coated onto platinized silicon substrates to form a film
- Films are pyrolyzed to remove any organics still present
- This process repeats until the desired thickness.
- Crystallization is undertaken to crystallize the films to form the perovskite phase




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

# Processing: Crystallization

- Fluorite phase stable ~500°C
- Perovskite forms above 500°C.
- Complete transformation of the film to perovskite is complete at ~600°C
- (100) and (111) textures are preferred for different applications, e.g. pyroelectric sensors or ferroelectric memories
- It is desirable to have control of final film texture in these films

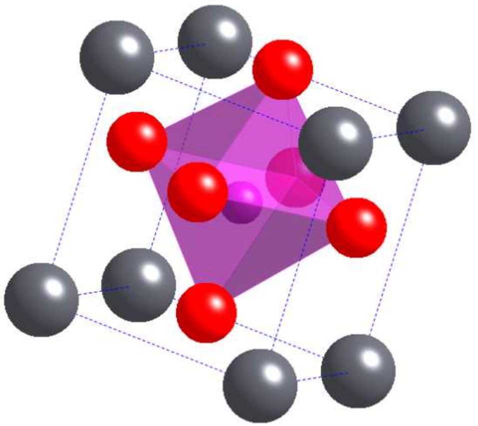



G. L. Brennecka *et al.* J. Am. Ceram. Soc. 93 (2010) 3935.

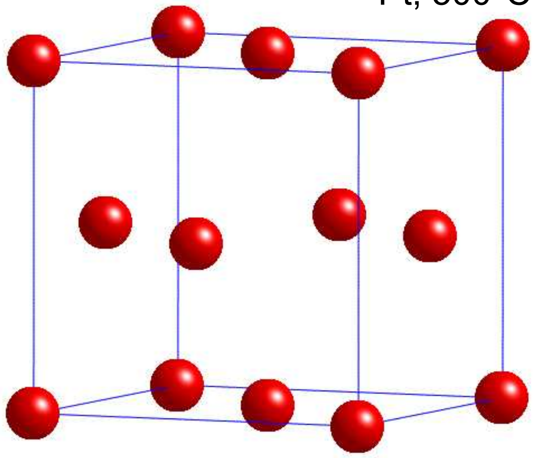
# Processing: Texture Development

- Factors affecting final film texture are poorly understood.
- Some determining factors include:
  - Heating rate
  - Adhesion layer
  - Film stress
  - Formation of intermediate/transient phases during crystallization, e.g. $Pt_xPb$

$a_{PbTiO3,\ 500°C}$ = 3.96 A

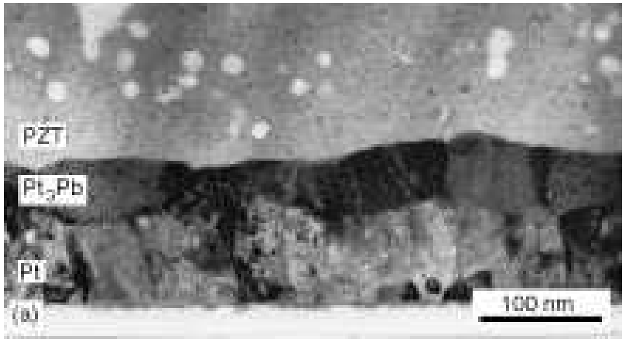


$a_{Pt,\ 500°C}$ = 3.94 A



# Processing: Texture Development

- The intermediate phases present in the thin film during perovskite nucleation (e.g., $Pt_xPb$, Fluorite) are believed to have a direct impact on the final texture by:
  - seeding specific orientations
  - making conditions favorable for a specific orientation, or
  - transforming into perovskite

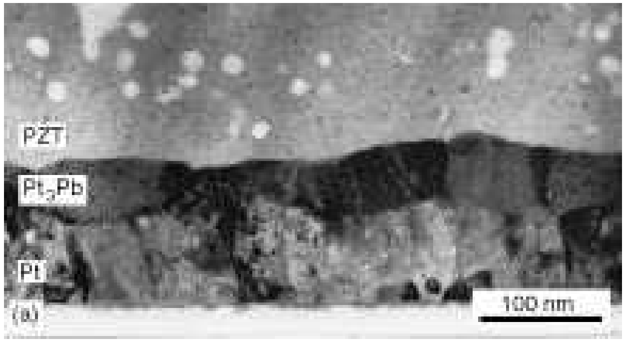



$Pt_xPb$ phase forms at the interface of the Pt electrode and the thin film.[5]

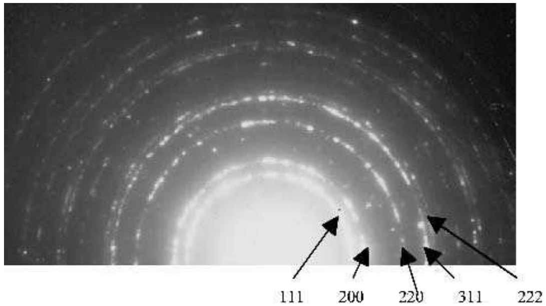
UF UNIVERSITY of FLORIDA

# Processing: Texture Development

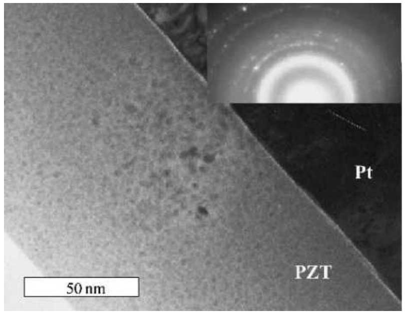
- $Pt_xPb$: (111) texture proposed to be due to nucleation of perovskite on $Pt_xPb$[3]
- Fluorite crystallinity: well crystallized fluorite leads to (111) texture[4]
- Ti from adhesion layer: $Pt_3Ti$ [6] and $TiO_2$ [7] seeds at the film-Pt interface lead to (111) texture




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




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

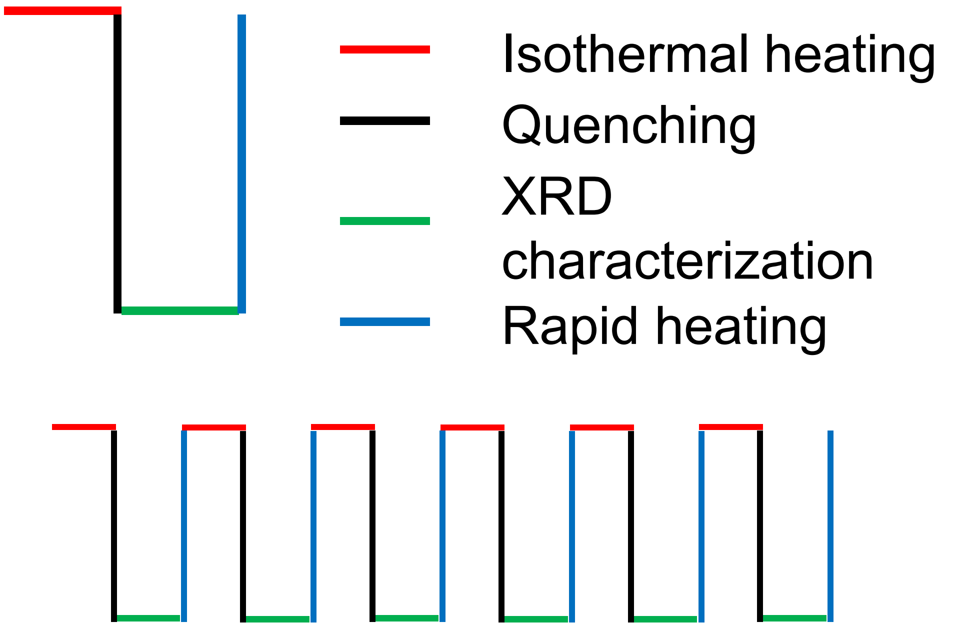



Pyrolysis: 450°C, 2 min
(100) texture

[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.

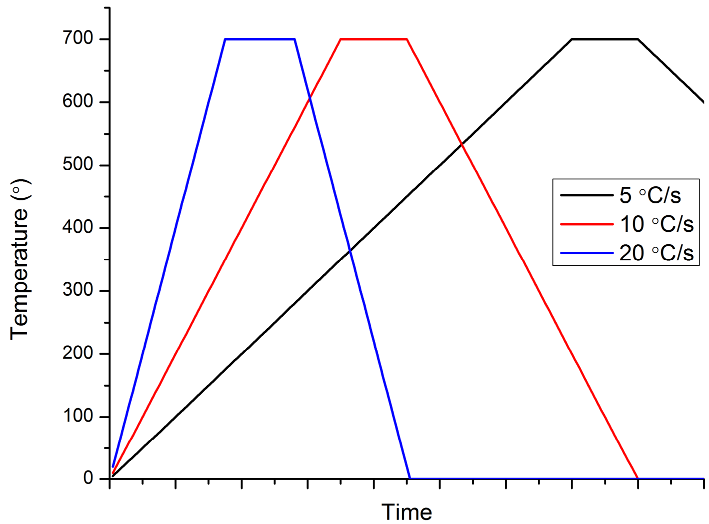
# Typical approaches for characterization of texture and phase

## Typical experimental methodologies




Repeated until the thin film completely crystallizes

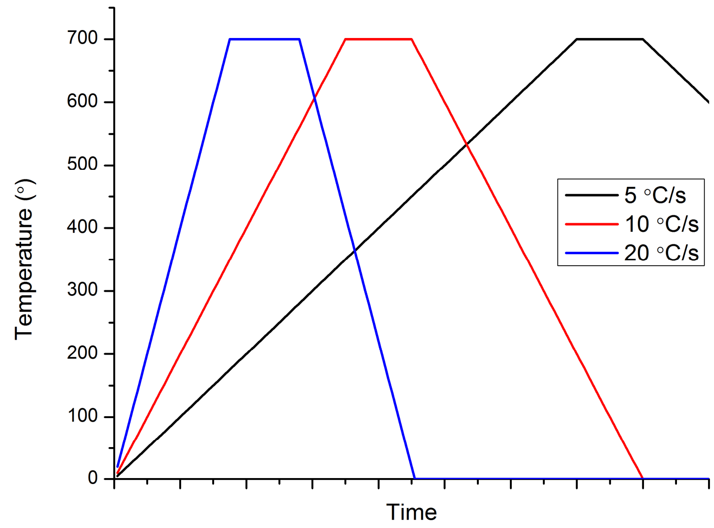
## Actual processing conditions



# Objective of present investigation

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

Actual processing conditions

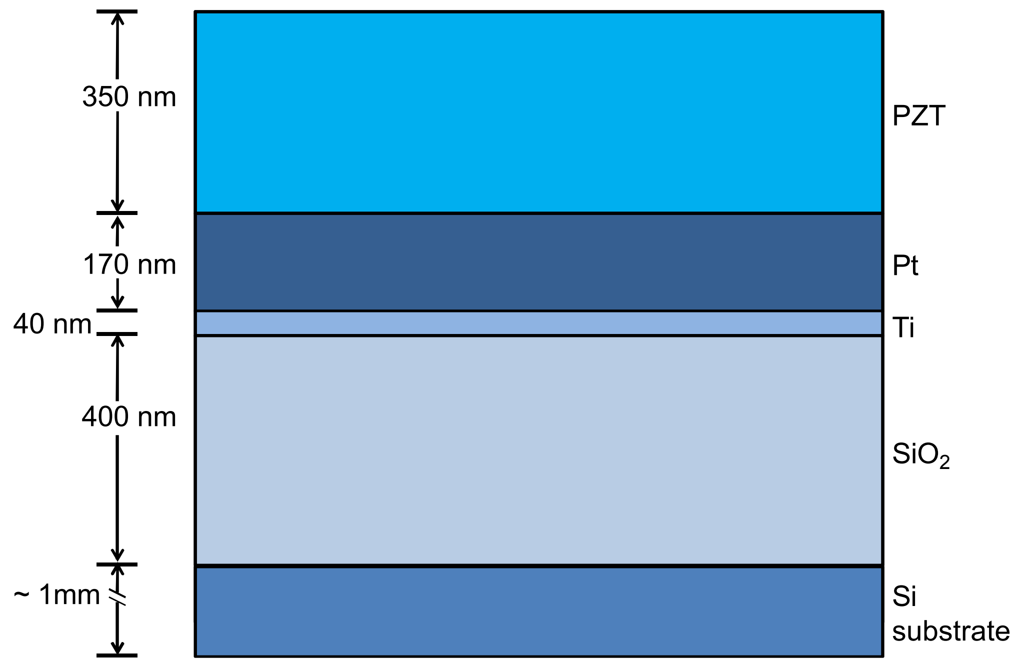


# Outline

1. Introduction
   – What we already know about processing, texture, characterization, etc.
   – Objective of present investigation (*in situ* crystallization)
2. Experimental Technique 1:
   – Laboratory X-ray Diffraction of PLZT±20%Pb
3. Experimental Technique 2:
   – X-ray Diffraction using Synchrotron of PZT±10%Pb
4. Conclusions

# Experimental – Synthesis

- PLZT solutions with La/Zr/Ti ratios of 6/52.2/46.3 prepared through IMO route[9]
- Some with 20% Pb-excess or 20% Pb-deficient
- Spin coat: 3000 rpm; 30s
- Films pyrolyzed at 300°C
- Crystallization done while diffraction patterns were measured (*in situ*)

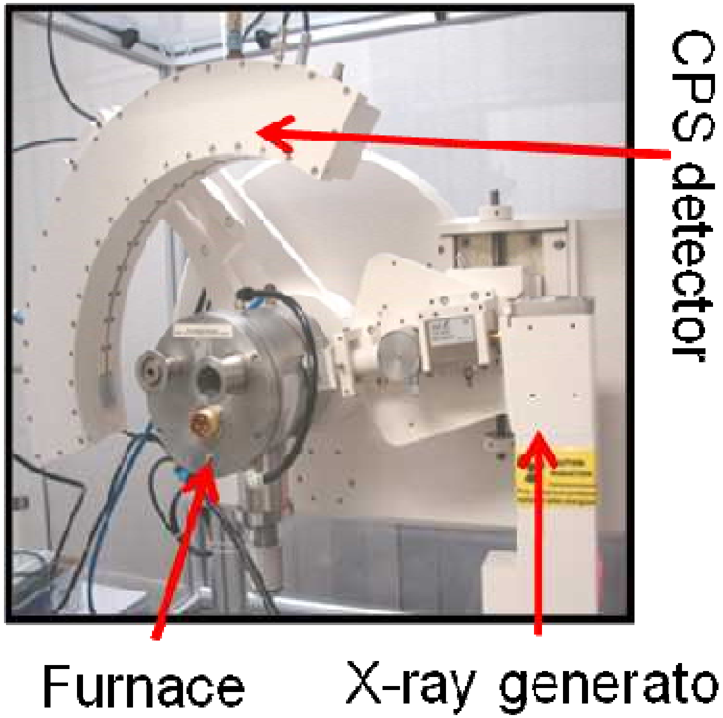



Film layer stack

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

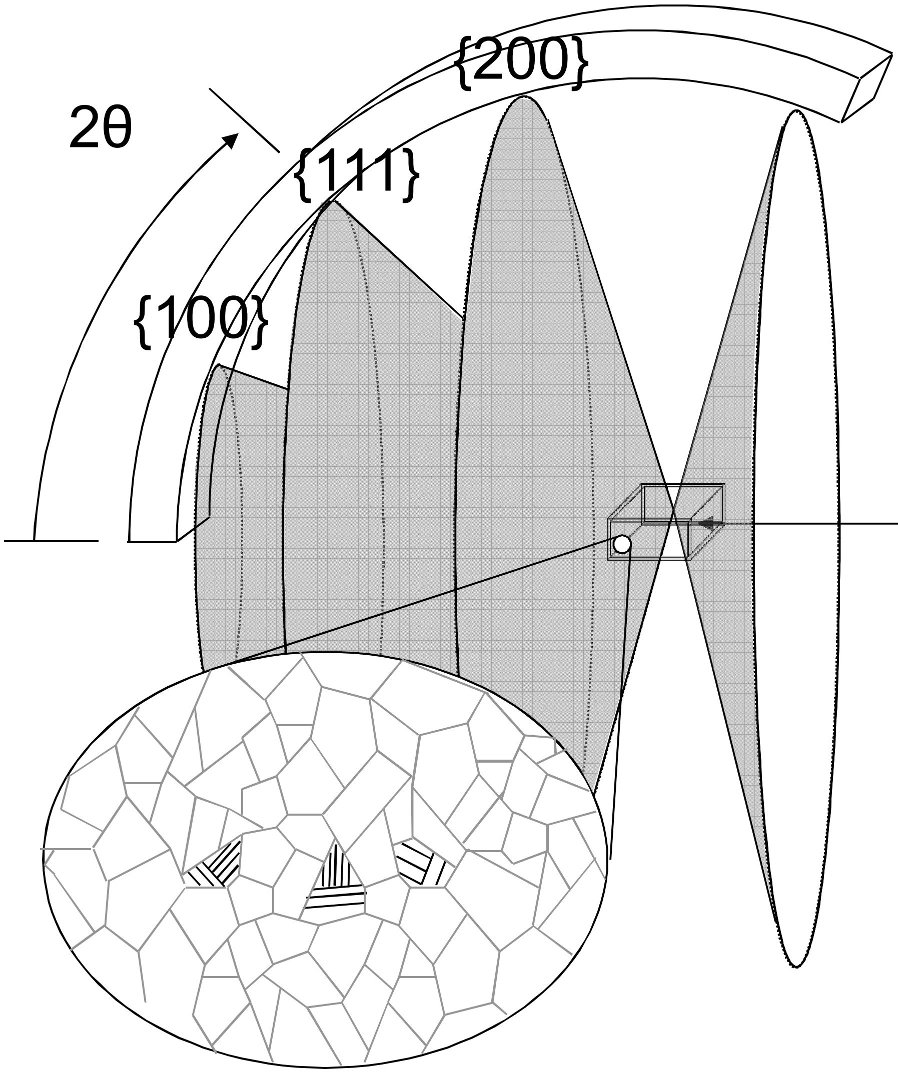
# Experimental – Laboratory XRD

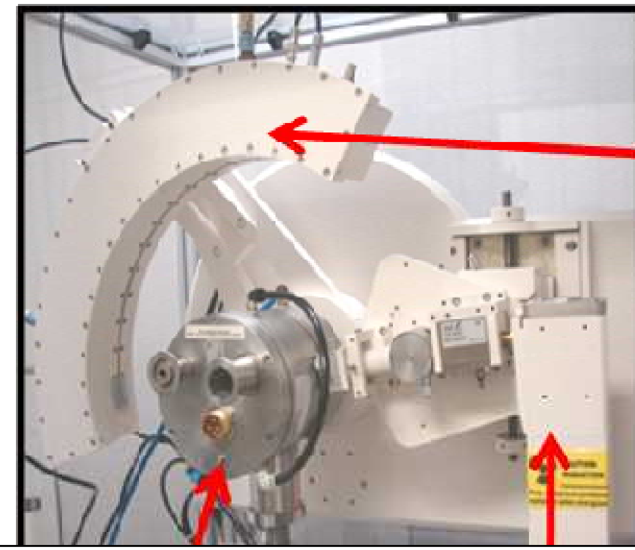
- Inel diffractometer with furnace attachment
- 1-D detector allows for rapid acquisition of diffraction data

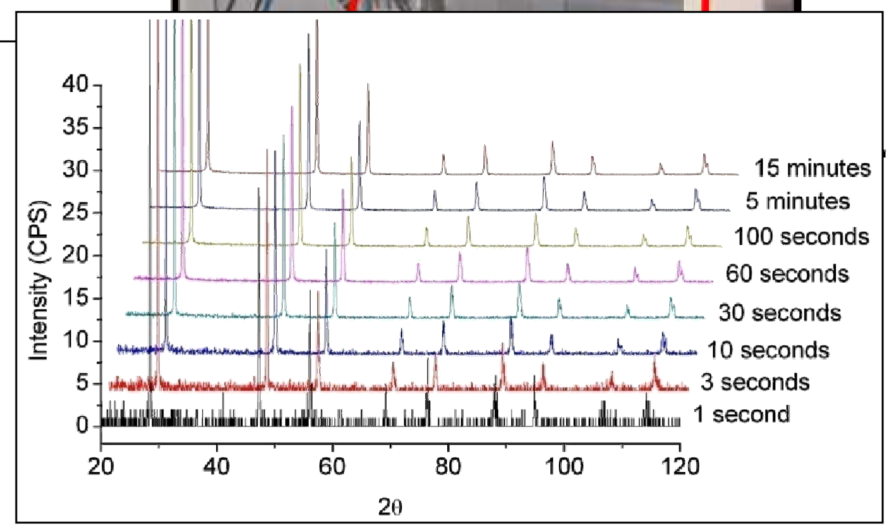



Nittala et al., *Journal of Materials Science 2011, 46, 2148-2154.*

# Experimental – Laboratory XRD

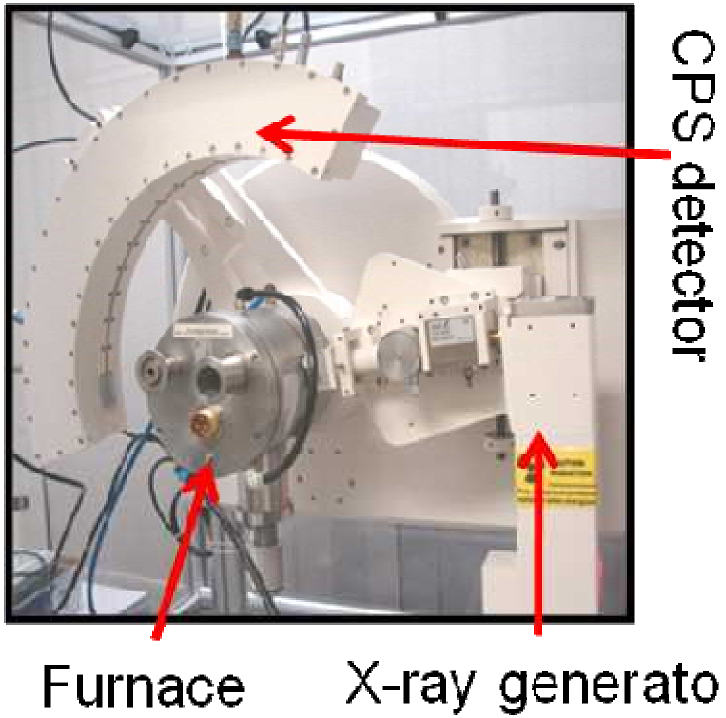


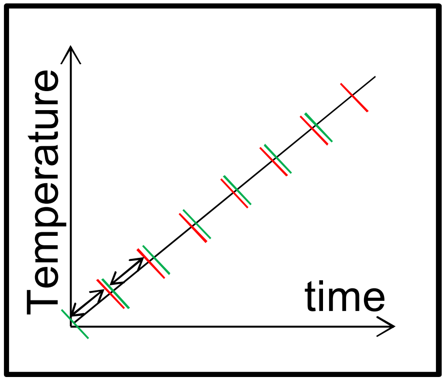



# Experimental – Laboratory XRD

- Inel diffractometer with furnace attachment
- 1-D detector allows for rapid acquisition of diffraction data
- Heating rate used is 5°C/min
- Diffraction patterns measured every 1 minute

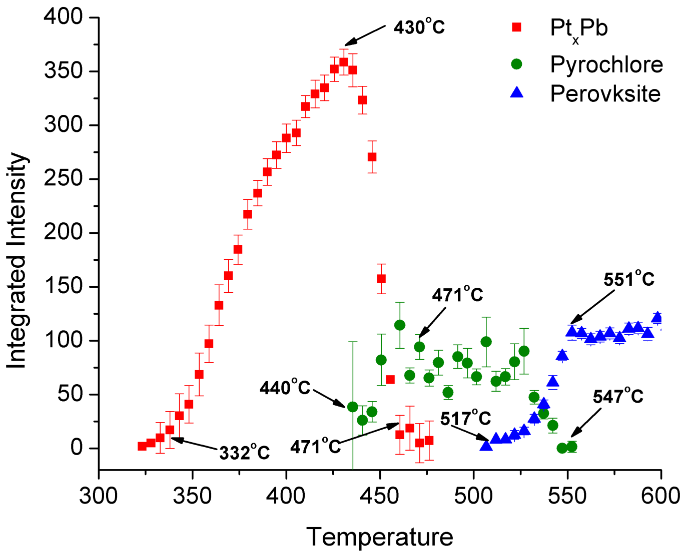


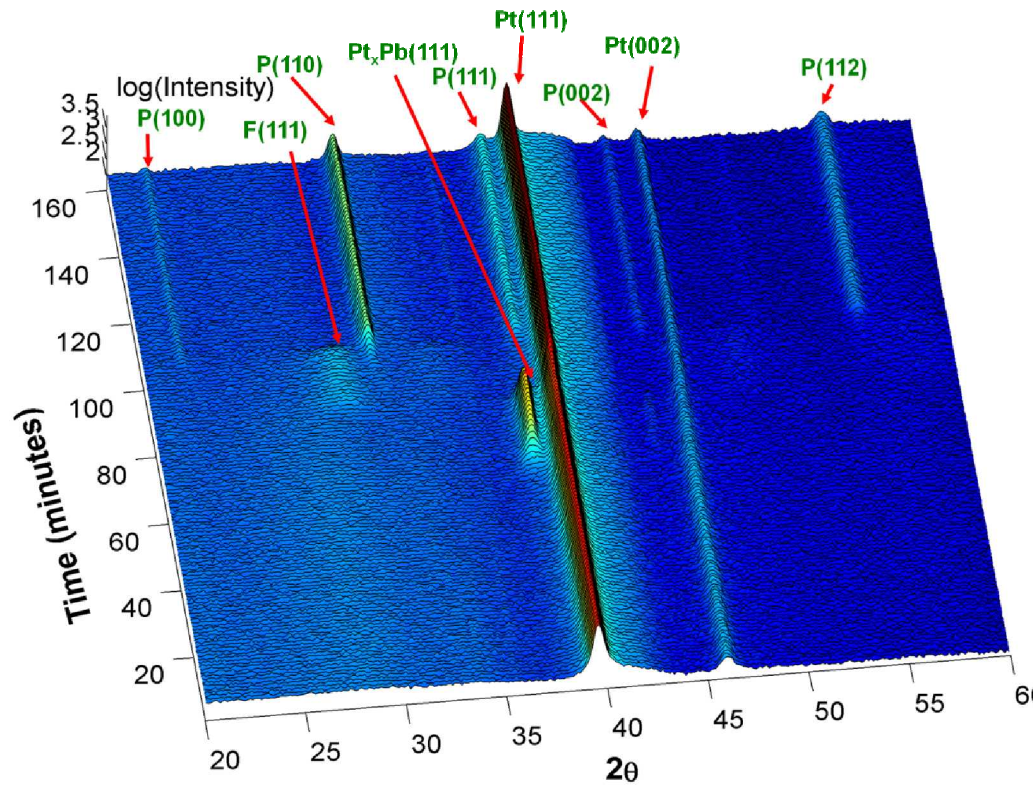




Nittala et al., *Journal of Materials Science 2011, 46, 2148-2154.*

# PLZT Films with Pb-excess

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



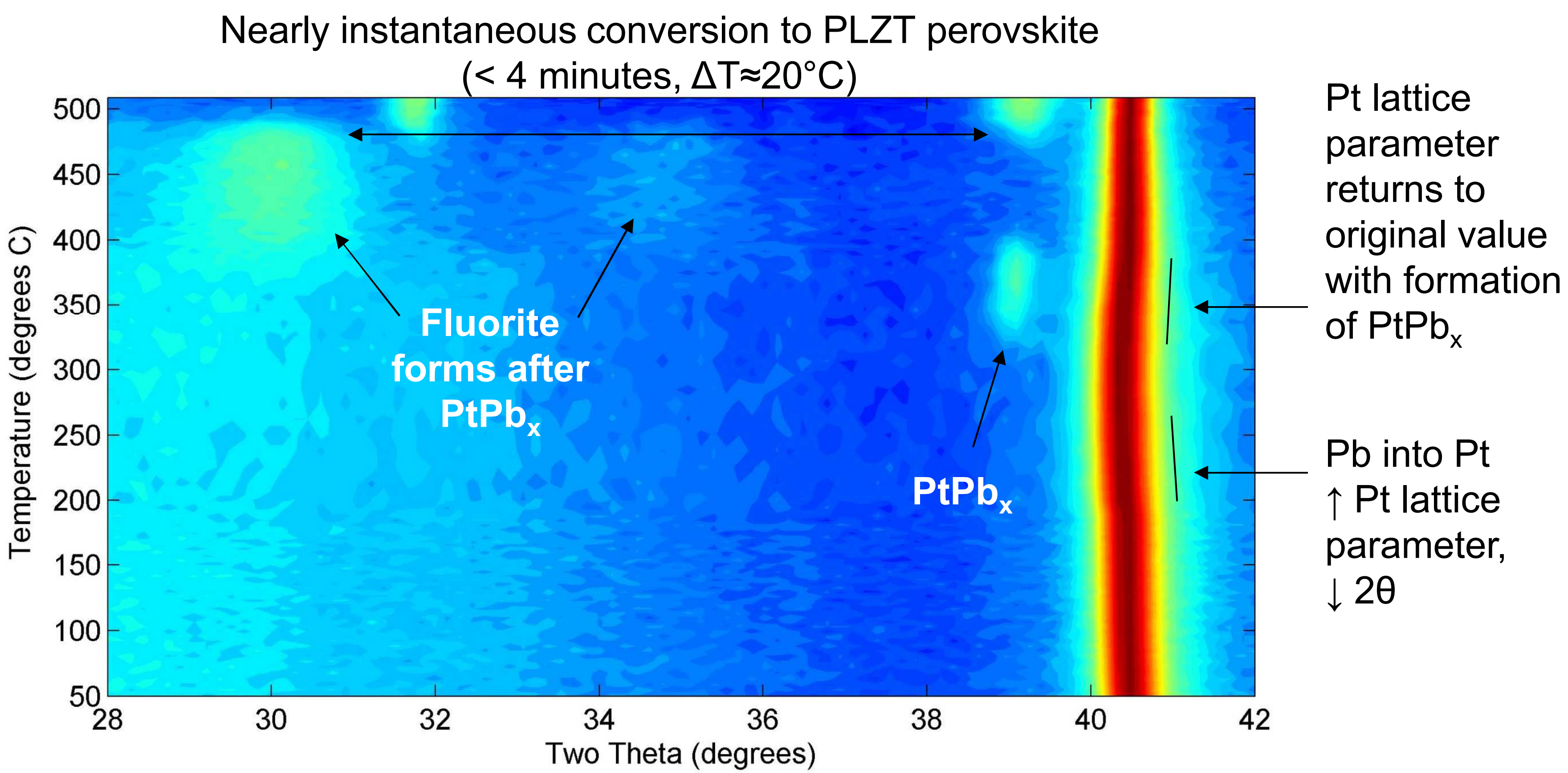




- Fluorite finally disappears and Perovskite (P) appears
- Result agrees with previous studies

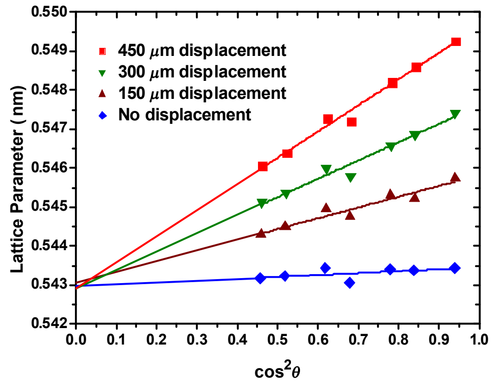
Nittala et al., *Journal of Materials Science 2011, 46, 2148-2154.*

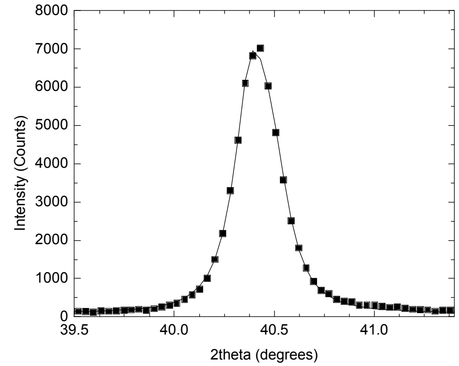
# PLZT Films with Pb-excess

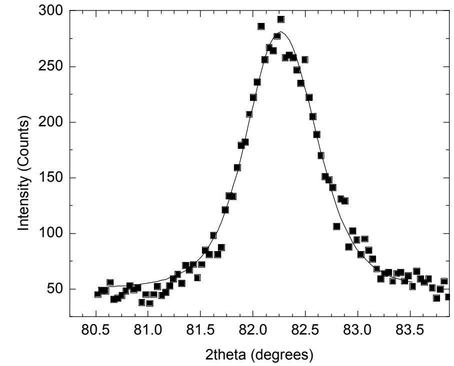
- $Pt_xPb$ is the first phase to form

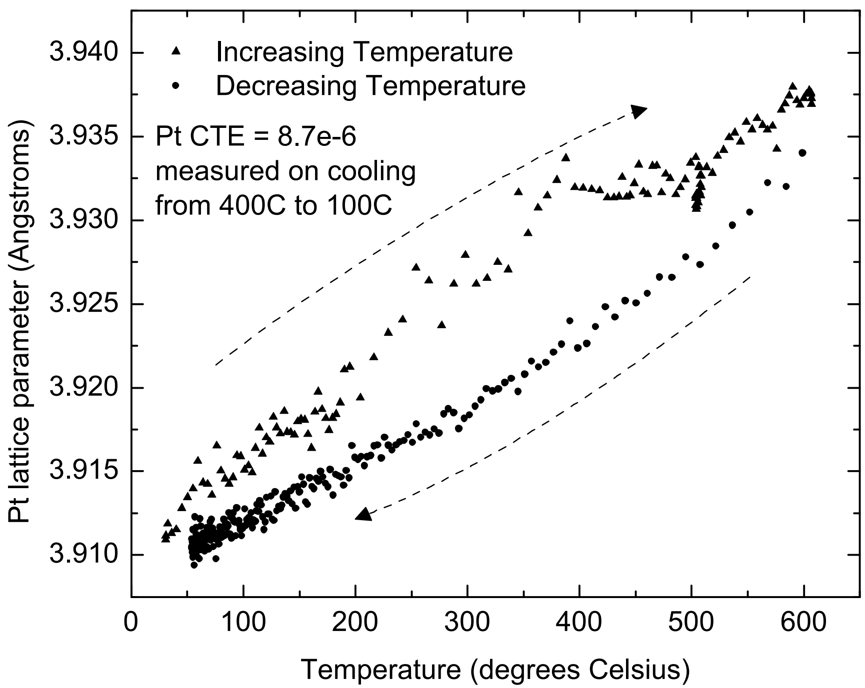


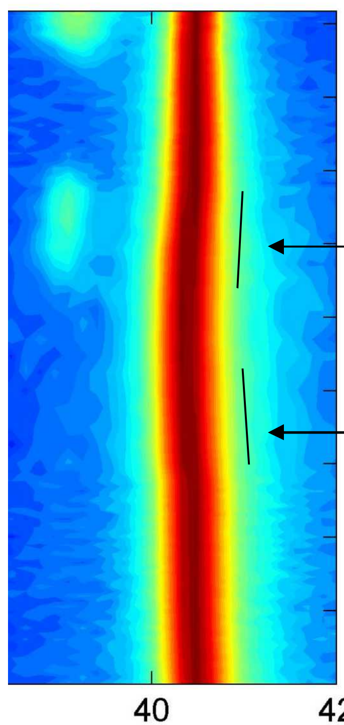
# PLZT Films with Pb-excess



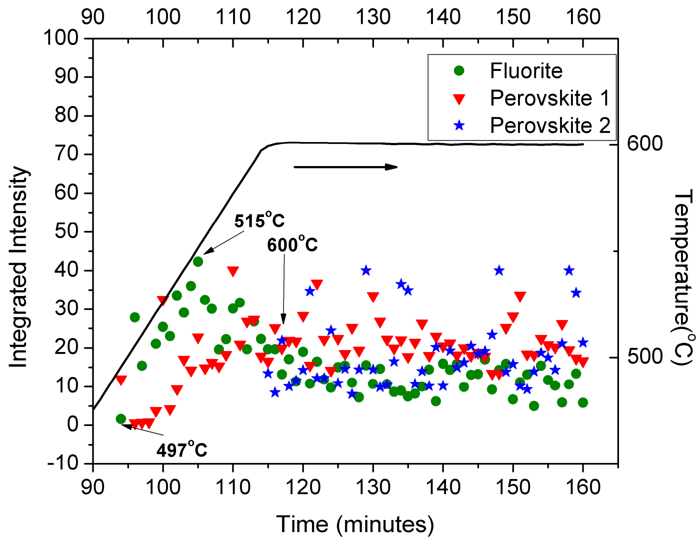



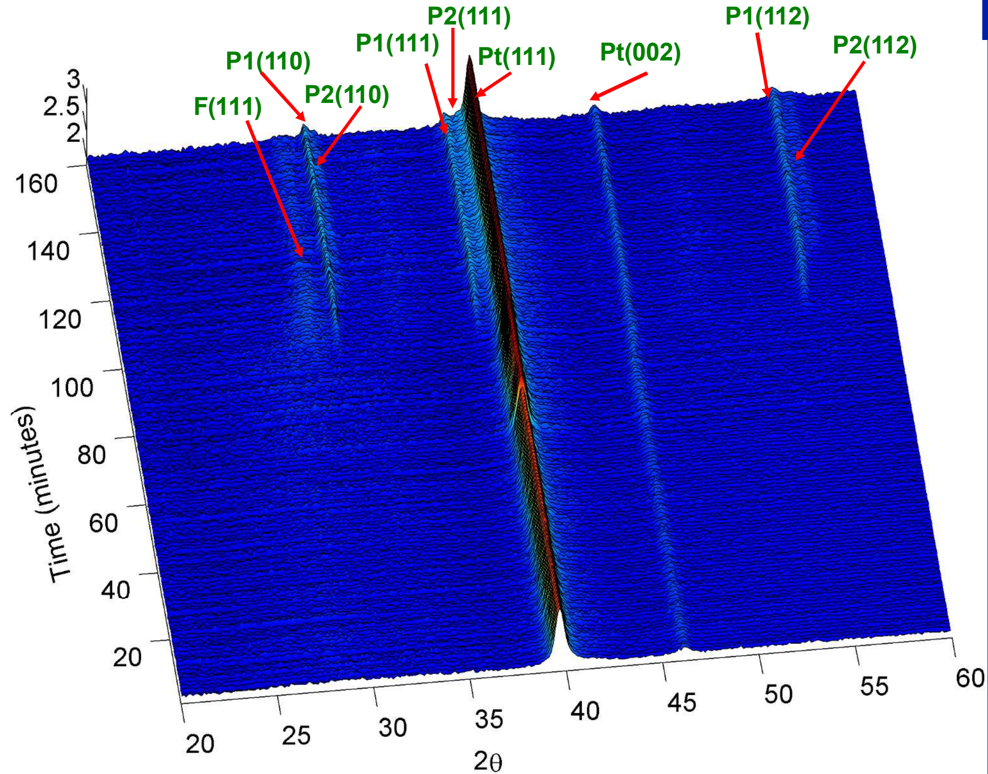

Pt lattice parameter returns to original value with formation of $PtPb_x$

Pb into Pt ↑ Pt lattice parameter, ↓ 2θ

# PLZT Films with Pb-deficient

- Fluorite (F) and Perovskite (P1) phase form together at 515°C
- A secondary perovskite phase (P2) forms upon holding at 600°C

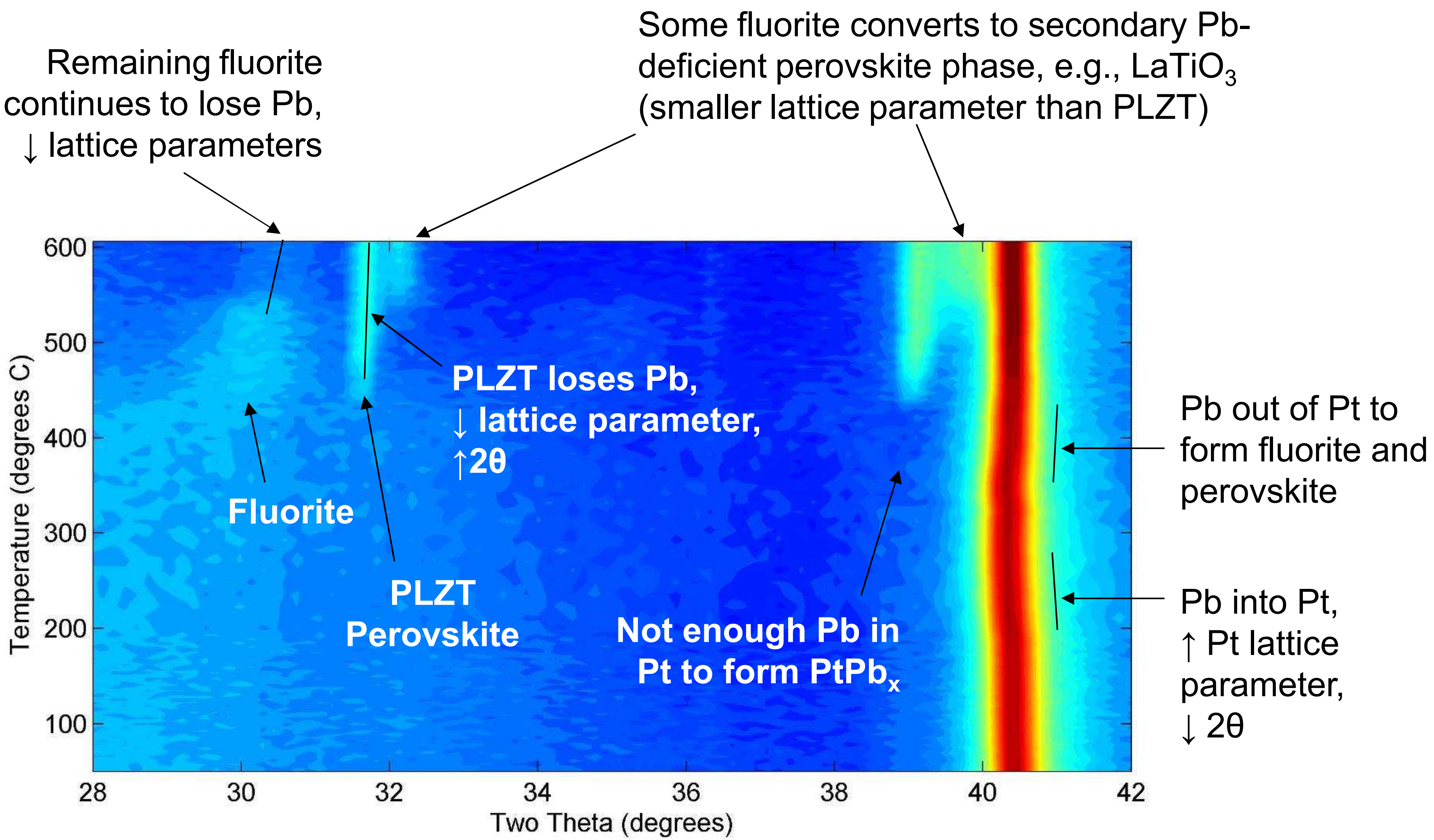



- No $Pt_xPb$ phase observed to form

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

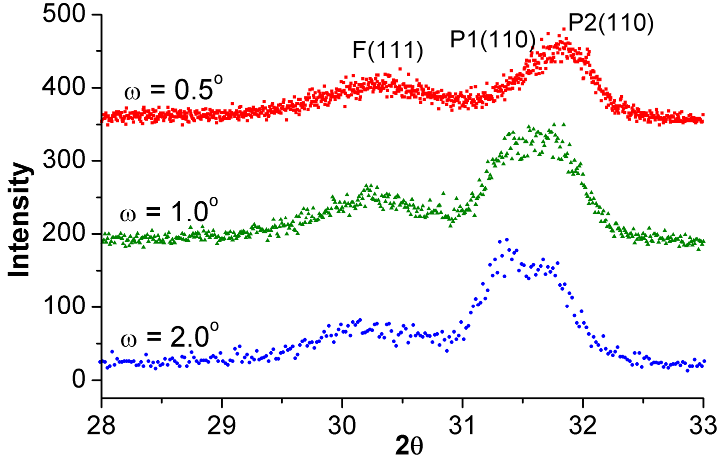
# PLZT Films with Pb-deficient

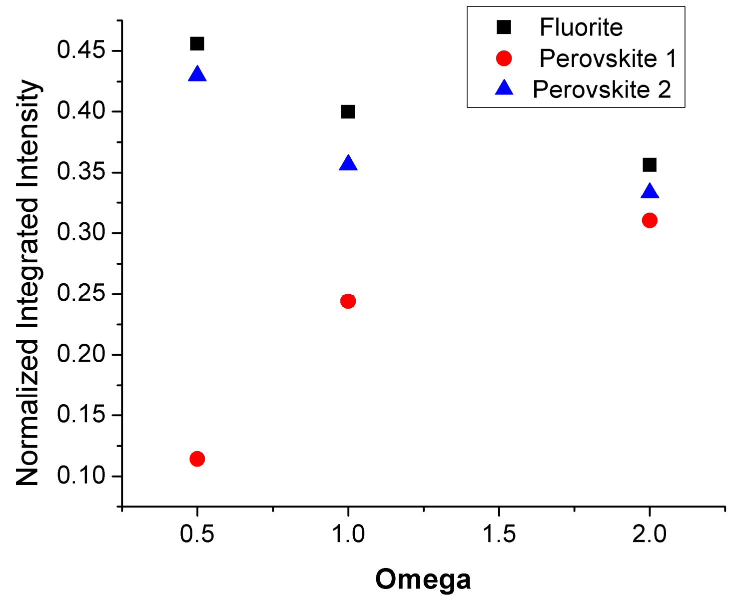


UF UNIVERSITY of FLORIDA

# PLZT Films with Pb-deficient

GIXRD



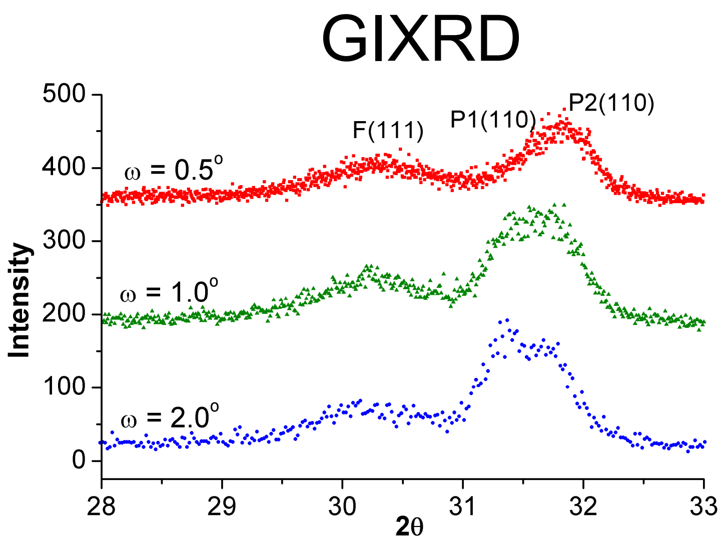



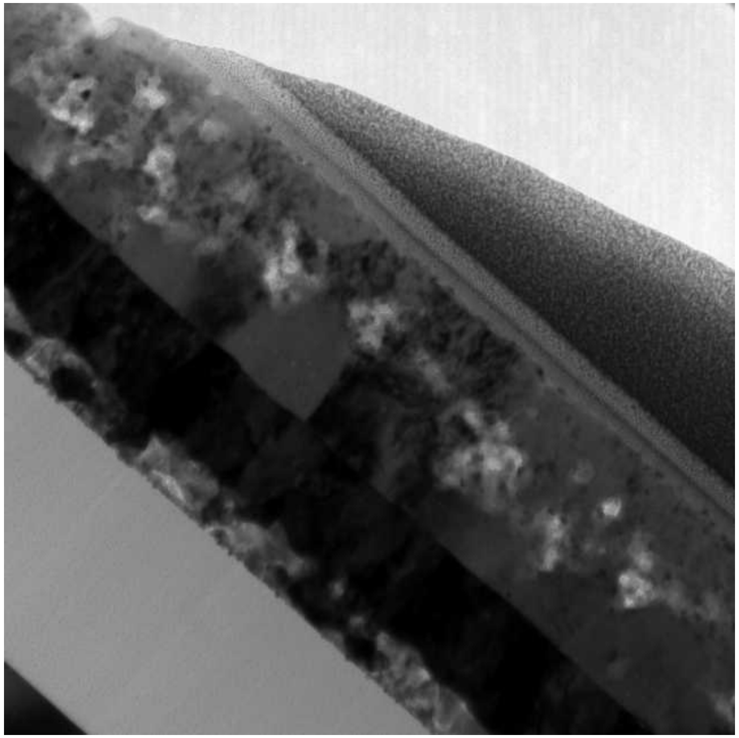

- Secondary Perovskite (P2) phase increases at shallow incidence angles
- Secondary Perovskite (P2) and Fluorite (F) phases increase towards the surface
- As perovskite nucleates and grows from the bottom, Pb-deficient material is pushed toward the top, resulting in the Secondary Perovskite (P2) phase with a lower lattice parameter and the defect-tolerant Fluorite phase.

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

UF UNIVERSITY of FLORIDA

# PLZT Films with Pb-deficient

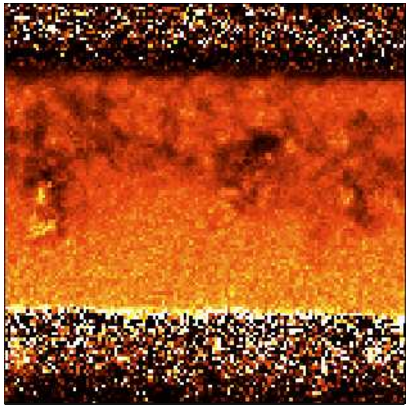


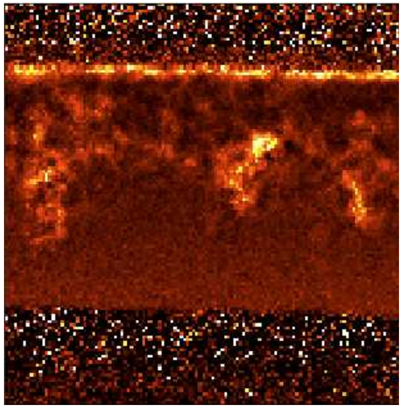
- Electron microscope image confirms secondary phase at the surface, likely Fluorite, and consistent with GIXRD measurements.

# PLZT Films with Pb-deficient

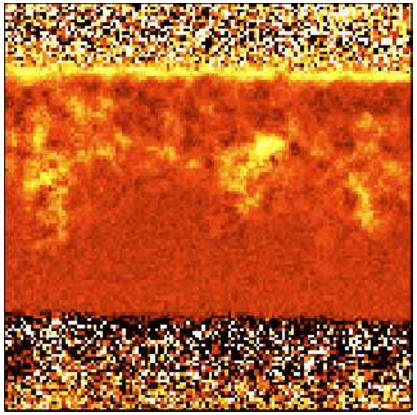
- Cation mapping across thickness of film using technique developed by Parish et al.*



Pb/(Zr+Ti)



Zr/Ti



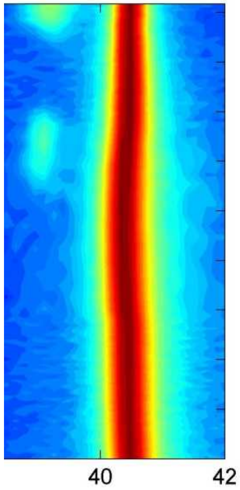
Zr+La

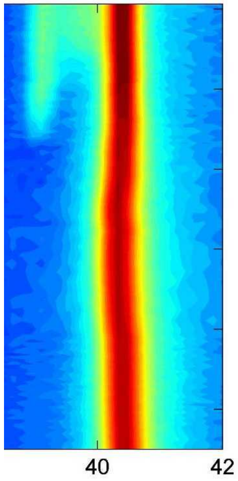
- No apparent contrast between secondary perovskite (P2) and fluorite (F) phase.
- Secondary perovskite phase is likely Pb-deficient (or Zr & La-rich), e.g. possibly $LaTiO_3$.
- Fluorite phase could be $La_2Zr_2O_{7-\delta}$, $(Pb,La)_2(Ti,Zr)_2O_{7-\delta}$, $(Ti,Zr)O_2$

*Parish et al., J. Am. Ceram. Soc., 91 [11] 3690–3697 (2008)

# Conclusions from 'slow rate' Laboratory XRD Measurements

- Pb-excess in starting solutions results in $Pt_xPb$ during crystallization and loss of Pb in film during crystallization
- Pb-deficiency reduces the interaction between Pt and Pb, though Pb still diffuses into Pt to some extent.
- Pb-deficiency results in remanent fluorite and secondary perovskite near the surface.
- Desirable to decrease reaction between film and electrode; especially for ultra thin films (10 – 50 nm)



UF | UNIVERSITY of FLORIDA

# Conclusions from 'slow rate' Laboratory XRD Measurements

- Limitations of laboratory X-ray measurements:
  - Low intensities
  - Low heating rates
  - No texture information
- Synchrotron X-ray diffraction is therefore needed, which can provide faster heating rates, higher intensities, and texture information

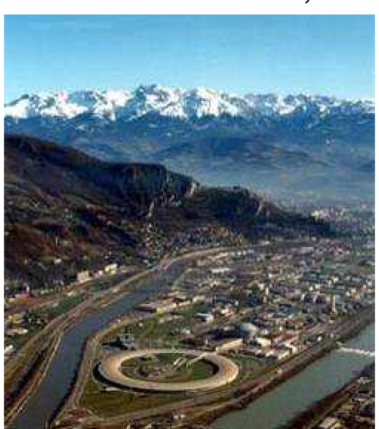
# Outline

1. Introduction
   – What we already know about processing, texture, characterization, etc.
   – Objective of present investigation (*in situ* crystallization)
2. Experimental Technique 1:
   – Laboratory X-ray Diffraction of PLZT±20%Pb
3. Experimental Technique 2:
   – X-ray Diffraction using Synchrotron of PZT±10%Pb
4. Conclusions

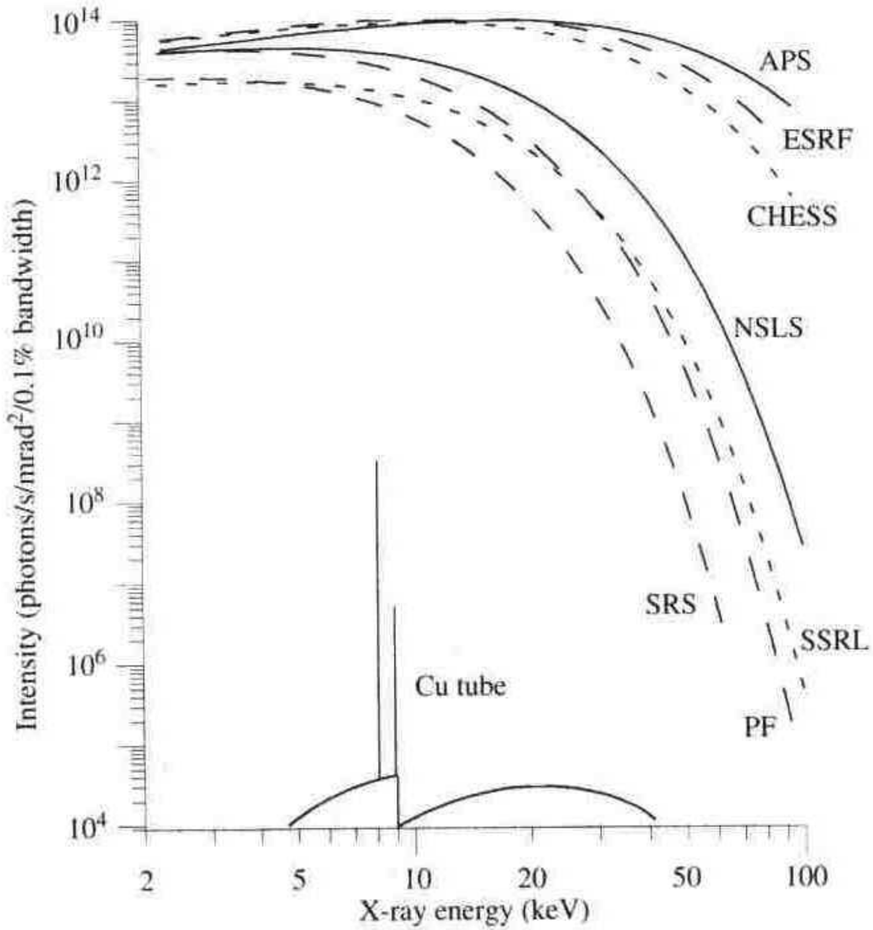
# Synchrotron Source

- Much higher intensities
- Can select any wavelength/energy available in spectrum
  - note discrete, characteristic energies of the Cu tube
- Higher energies can penetrate through an entire sample
  - →simple geometries & large sampling volume

*ESRF in Grenoble, France*



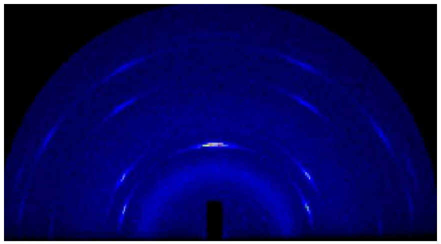
*APS, Argonne (Chicago), IL*


Stephens, ch. 4 in
Struct. Det. in Powder Diff. Data (2002).

UF UNIVERSITY of FLORIDA

# Experimental – Synchrotron source



Detector image

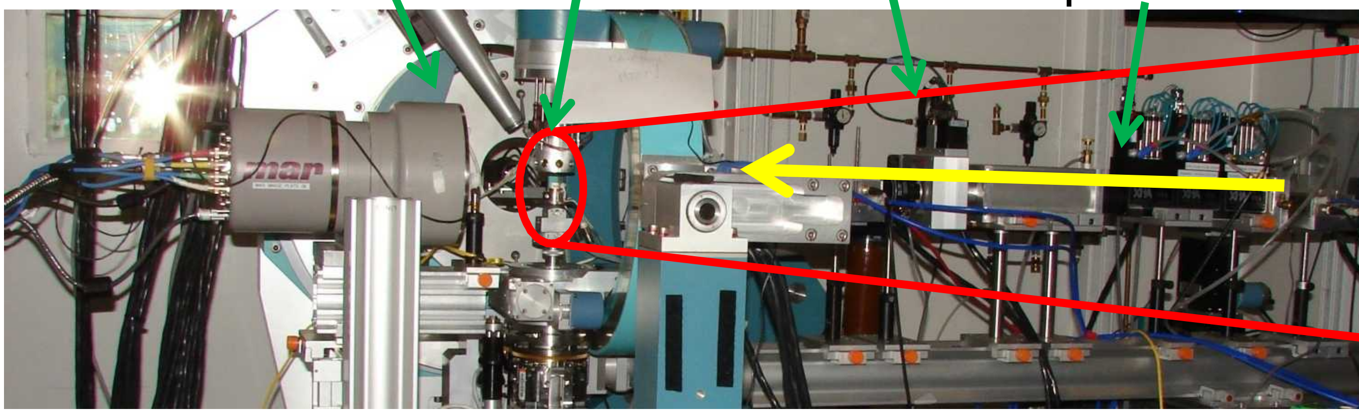
Detector

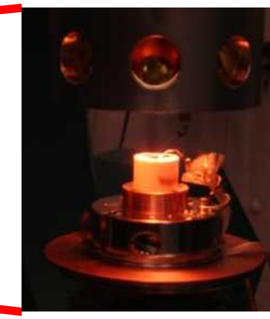
Sample/Stage

Shutter

X-ray beam path

Sample heated with IR lamp

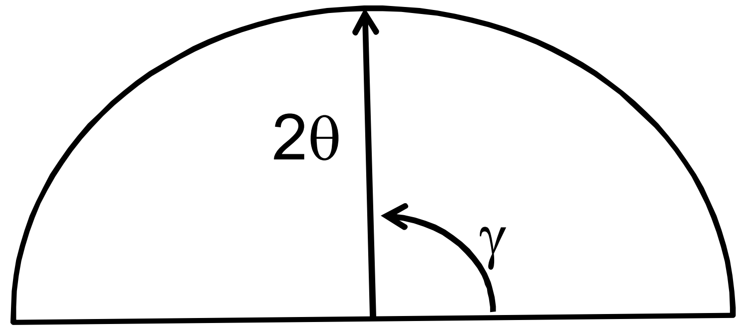


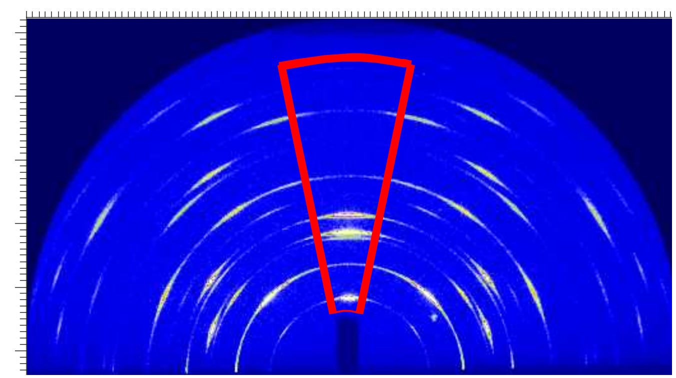



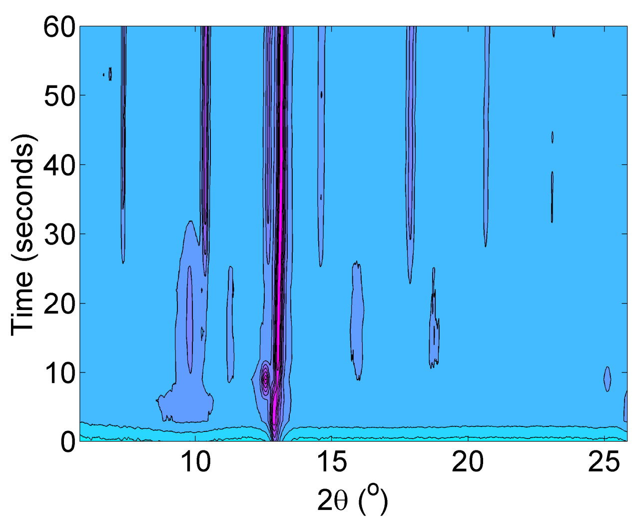
- Experiments were completed at Sector 6 at the Advanced Photon Source (APS) In collaboration with Dr. Douglas S. Robinson.
- Energy of ~32 keV.
- Heating rates varied between **~100 C/s to 0.5 C/s**.
- **2-D detector** allows for characterization of texture.
- Continuous diffraction patterns collected with **1 second acquisition time**.

# Experimental – Synchrotron source

- First representative output
- Diffraction intensities were integrated through a limited azimuthal ($\gamma$) range (85° - 95°) to generate $2\theta$ vs. Intensity data for each diffraction pattern

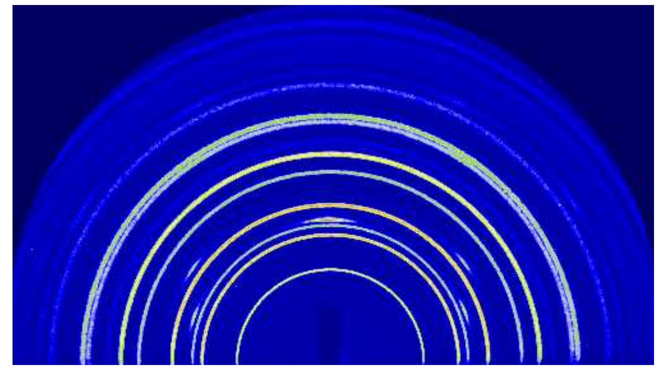


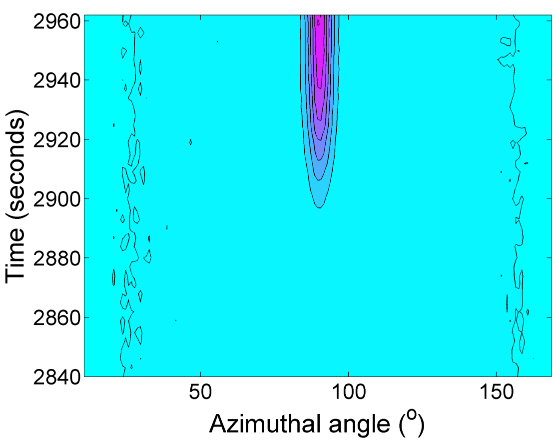


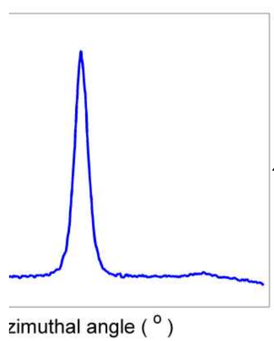
# Experimental – Synchrotron source

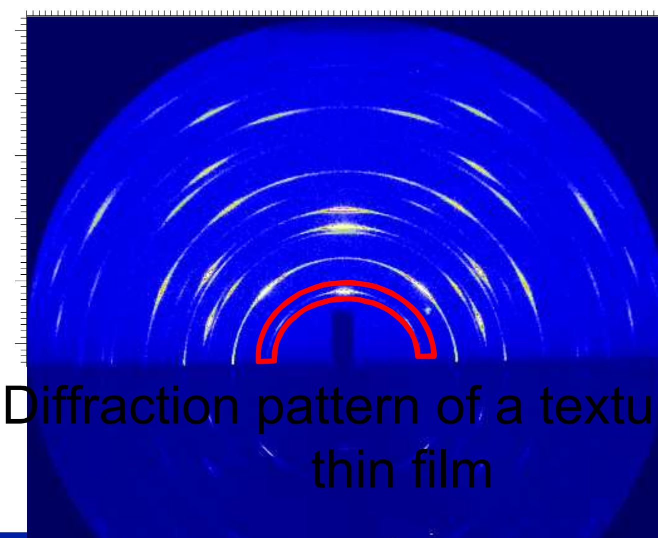
- Second representation output
- Intensity variation with $\gamma$ indicates texture.
- Intensity was integrated through specific 2θ (e.g., perovskite 100) to obtain intensity as a function of azimuthal ($\gamma$) angle



Alumina powder on substrate

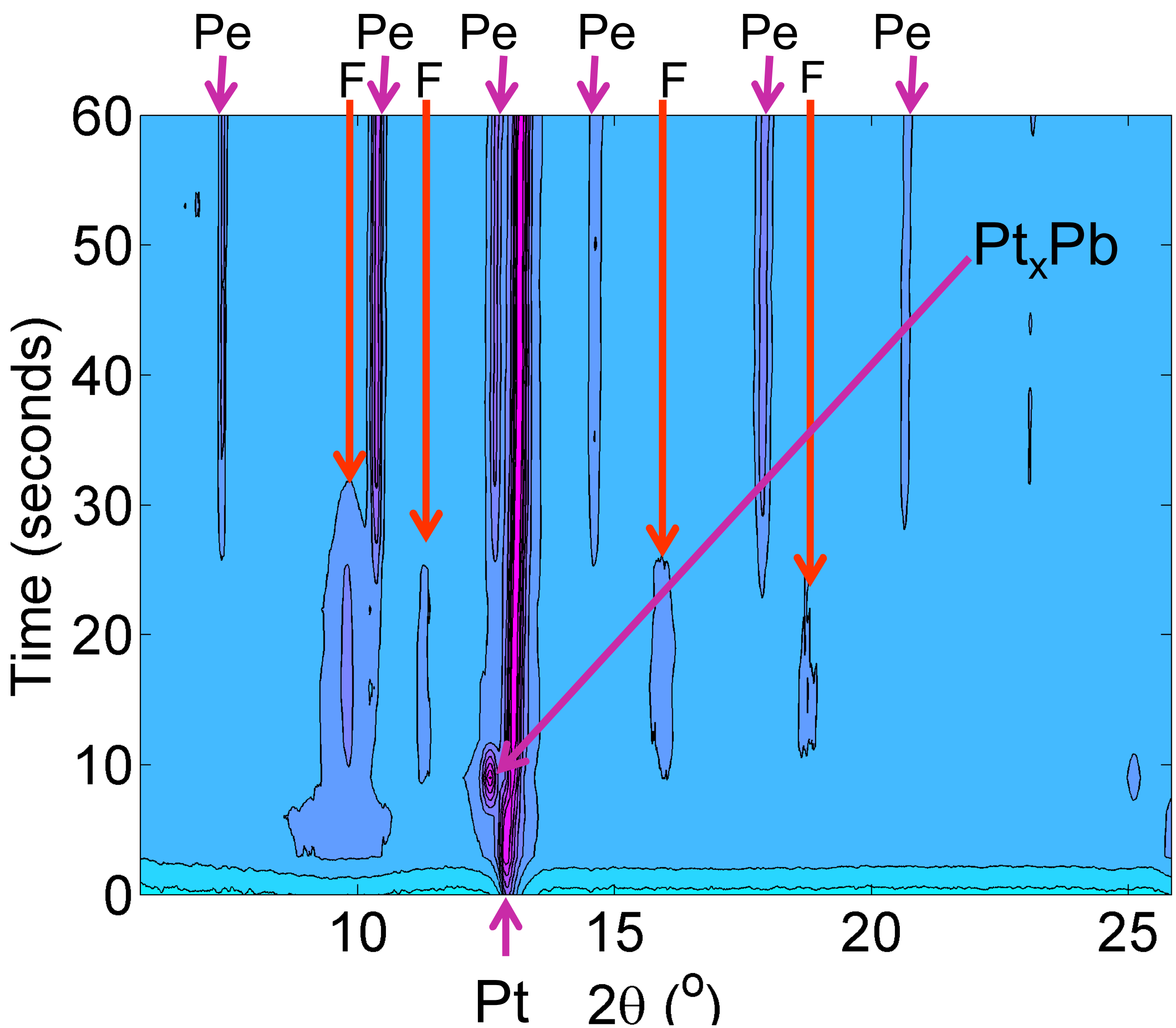


Diffraction pattern of a textured thin film

# Representative result for PZT(52/48) + 10% Pb-excess



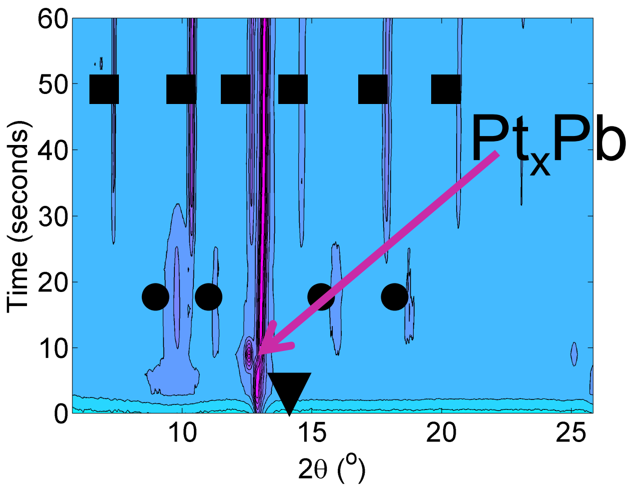

- Fastest heating rate: ~100°C/s
- **No overlap in $Pt_xPb$ and perovskite phases**
- Fluorite phase directly precedes perovskite phase

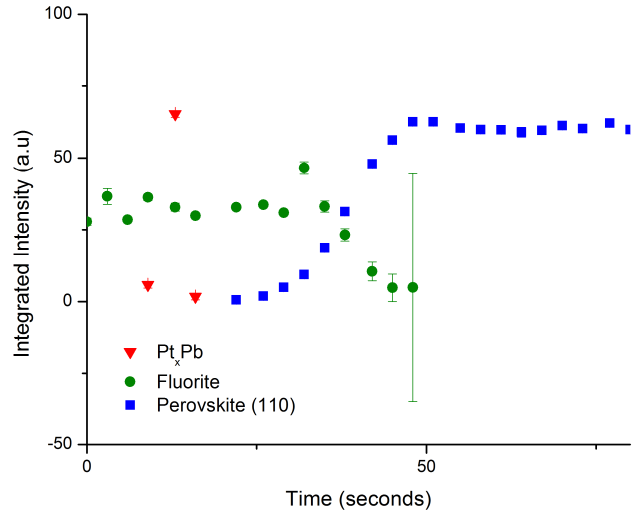
Pe: Perovskite
F: Fluorite

UF | UNIVERSITY of FLORIDA

# Heating rate influences phase evolution

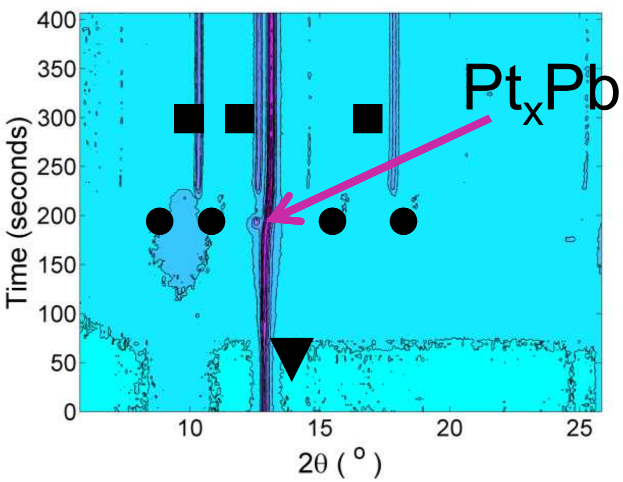
**~100°C/s**

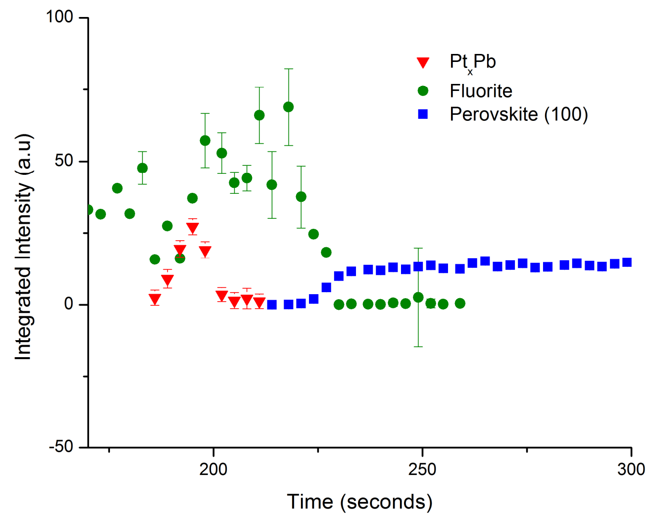



- No overlap in $Pt_xPb$ and perovskite phases

**~5°C/s**



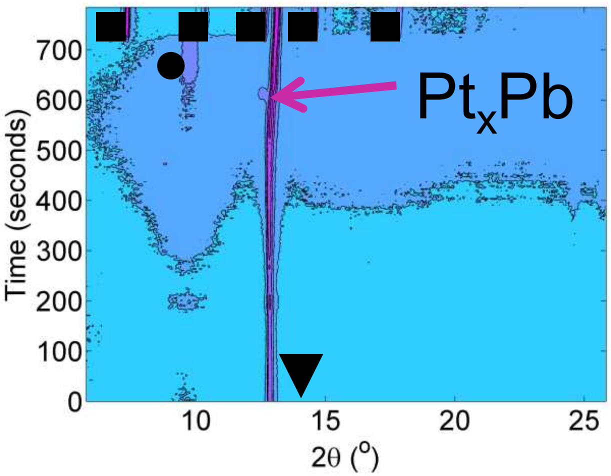

- Amount of $Pt_xPb$ formed decreases with heating rate

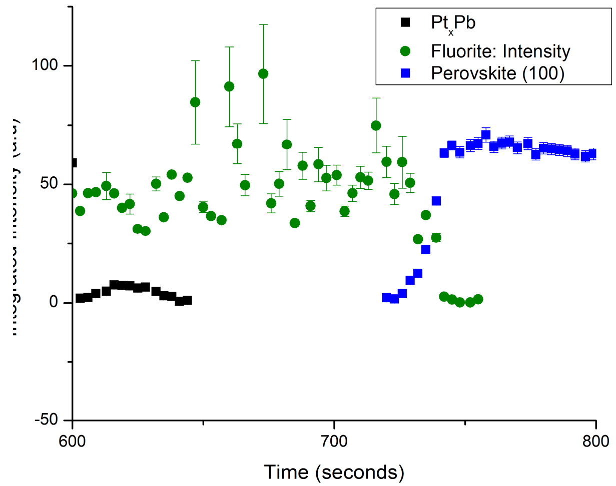
▼ Pt ■ Perovskite ● Fluorite

UF UNIVERSITY of FLORIDA

# Heating rate influences phase evolution

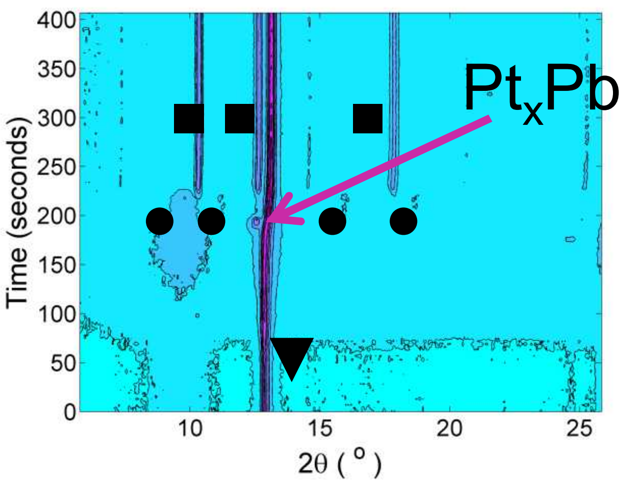
**~1°C/s**

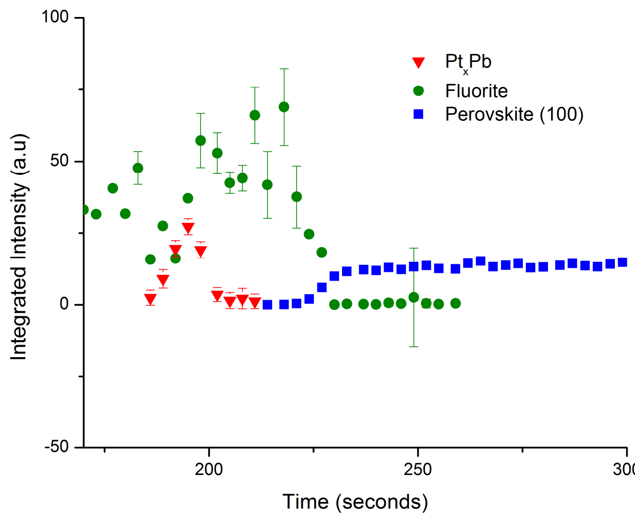



- Crystallinity of fluorite phase changes with heating rate

**~5°C/s**



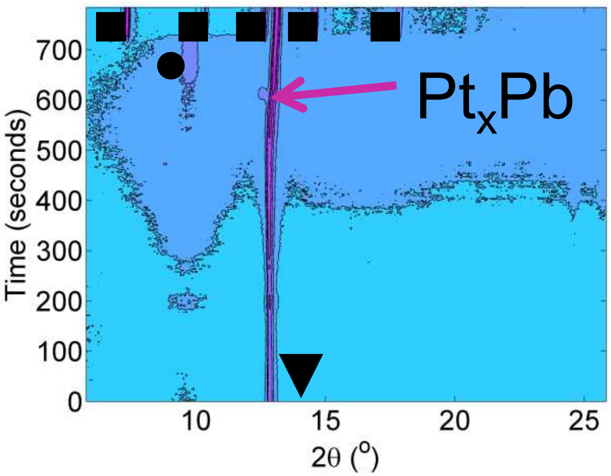



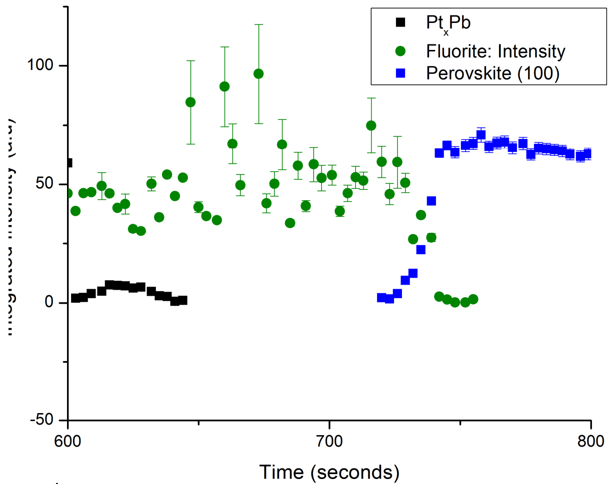

- Amount of $Pt_xPb$ formed decreases with heating rate

▼ Pt ■ Perovskite ● Fluorite

# Heating rate influences phase evolution

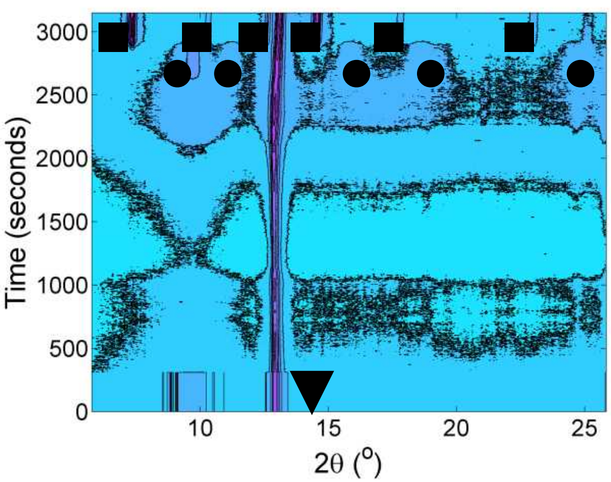
**~1°C/s**

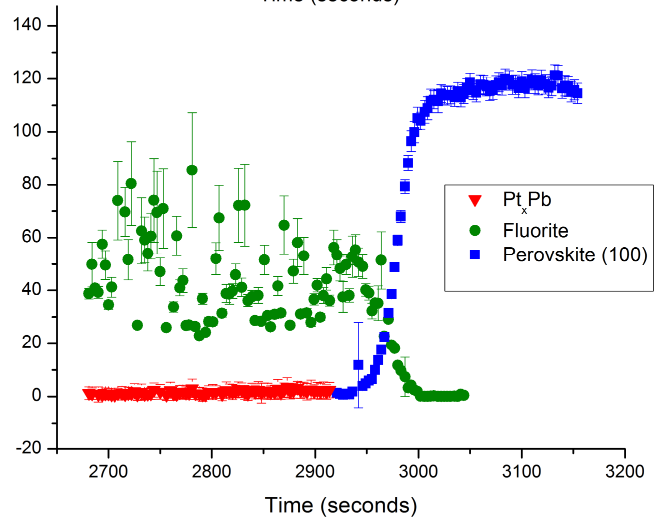



- Crystallinity of fluorite phase changes with heating rate

**~0.5°C/s**



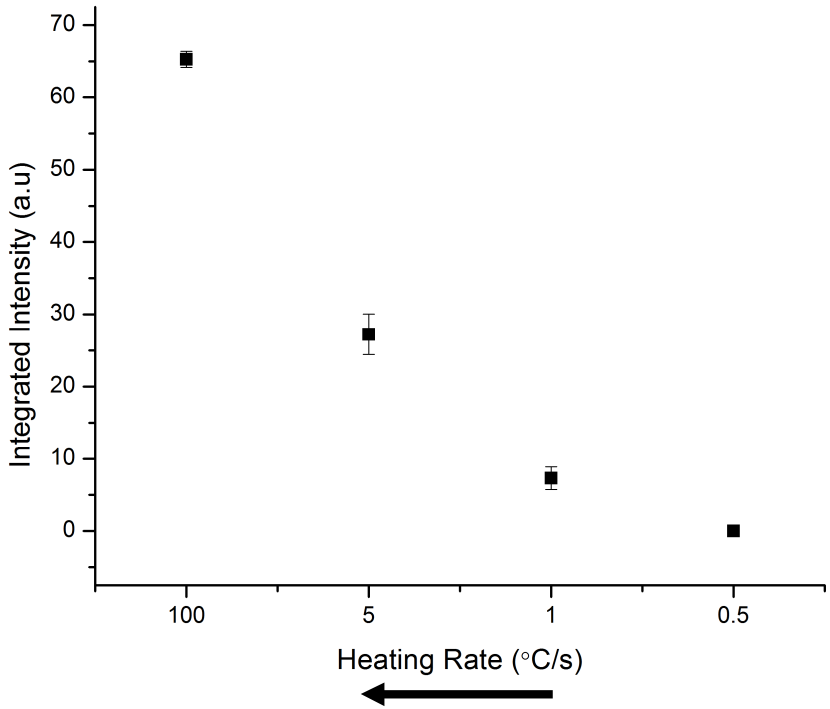




- No $Pt_xPb$ formation is observed

▼ Pt ■ Perovskite ● Fluorite

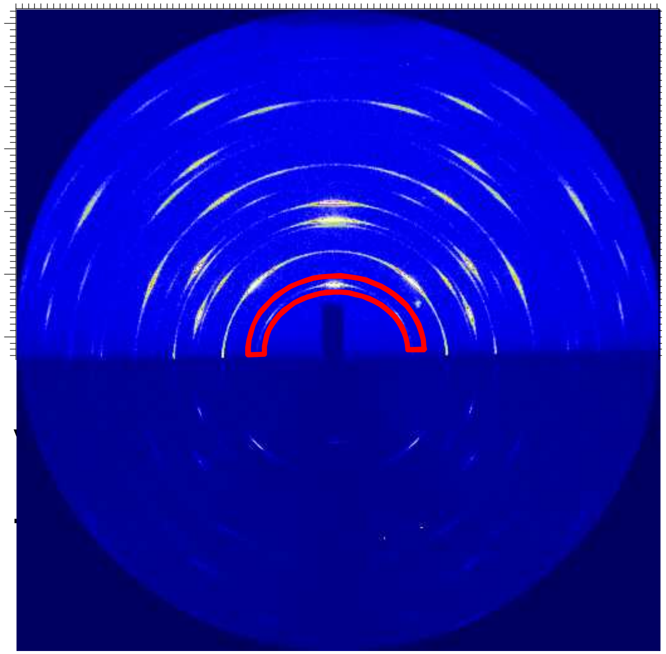
# Variation of $Pt_xPb$ with heating rate

- Maximum intensity of $Pt_xPb$ decreases with heating rate
- No $Pt_xPb$ observed to form in slowest heating rate
- Observed stability of $Pt_xPb$ is consistent with *ex situ* observations*
- No overlap is observed between the $Pt_xPb$ phase and the perovskite phase, indicating one probably does not template the other

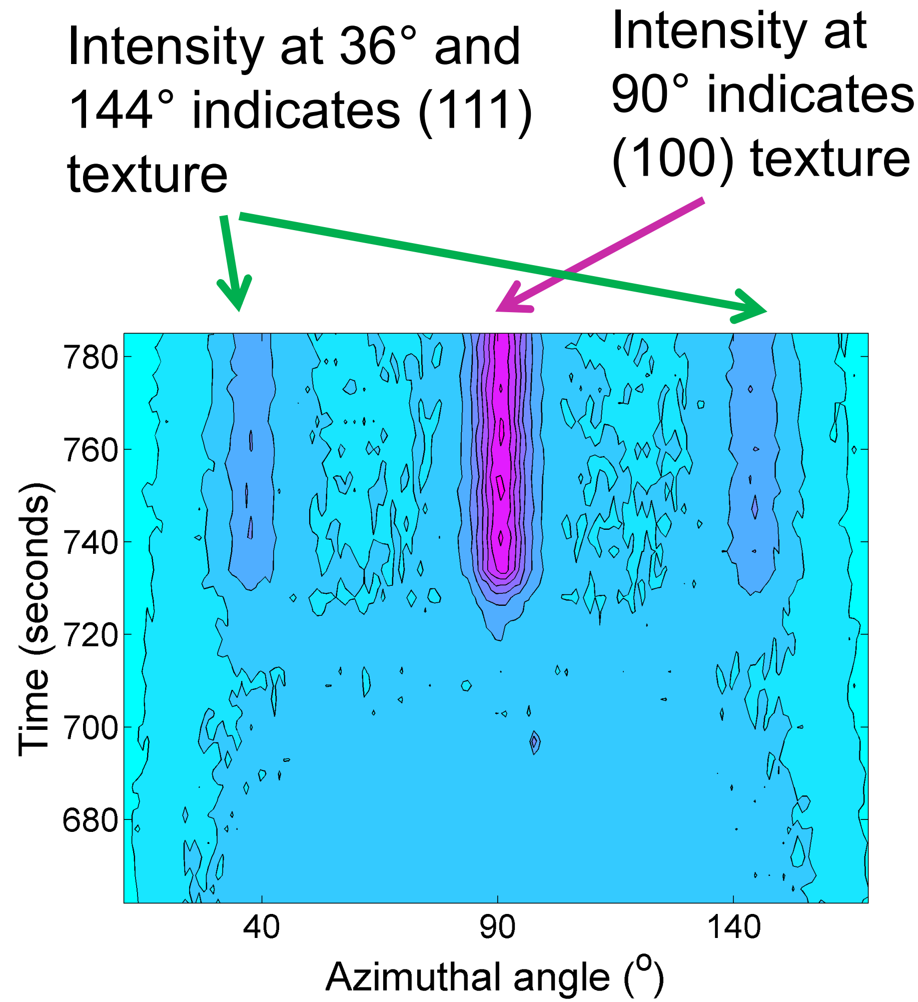



*S. Y. Chen and I. W. Chen, J. Am. Ceram. Soc. 77 (1994) 2332.

# Method of texture representation



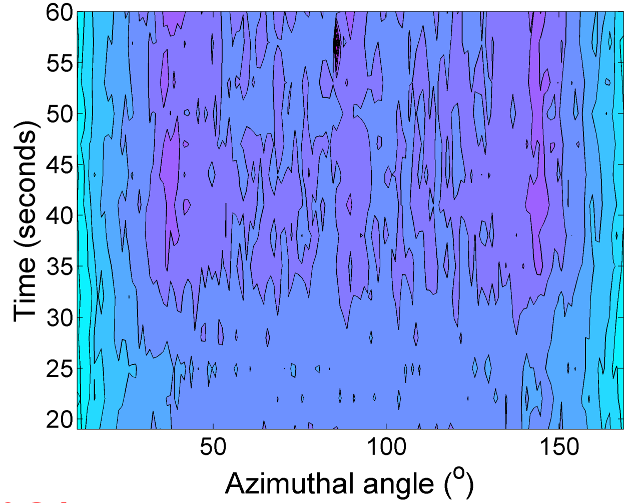
- against time.
- Intensity vs gamma data for the (100) peak is similar to that obtained through a typical $\chi$-scan.

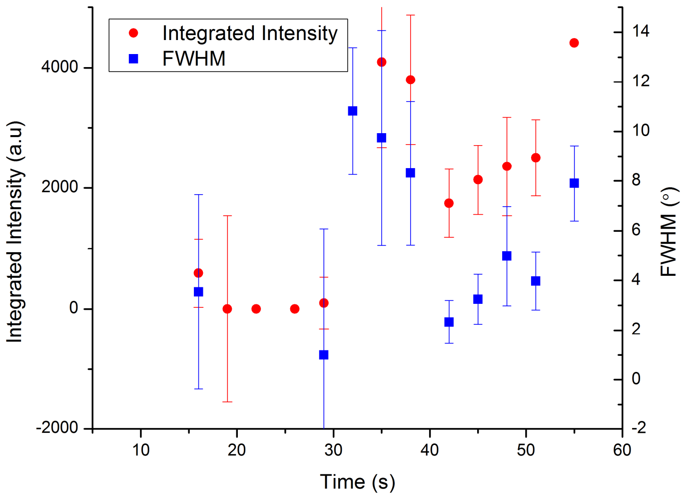


UNIVERSITY of FLORIDA

# Heating rate influences texture

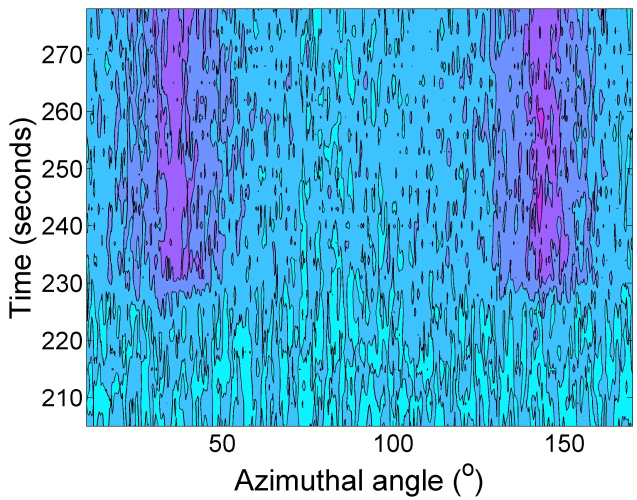
## ~100°C/s

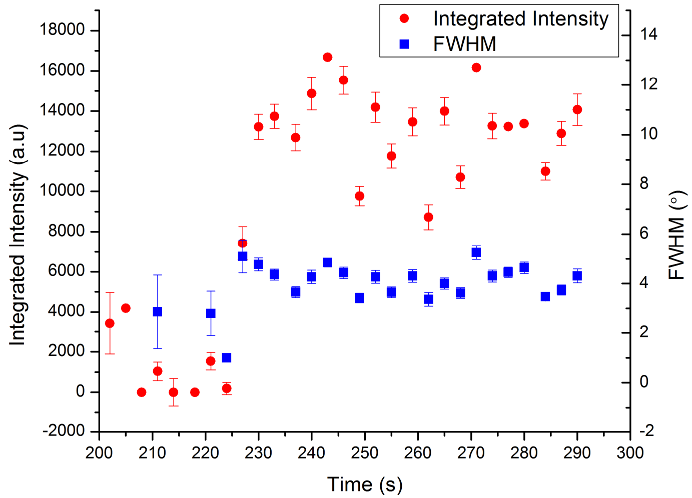



- No distinct trends in texture

## ~5°C/s

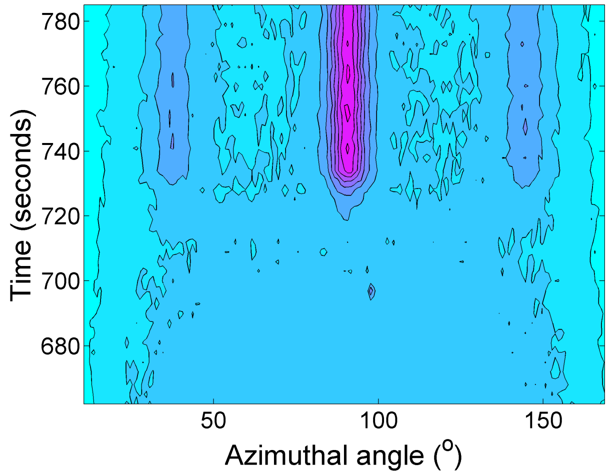


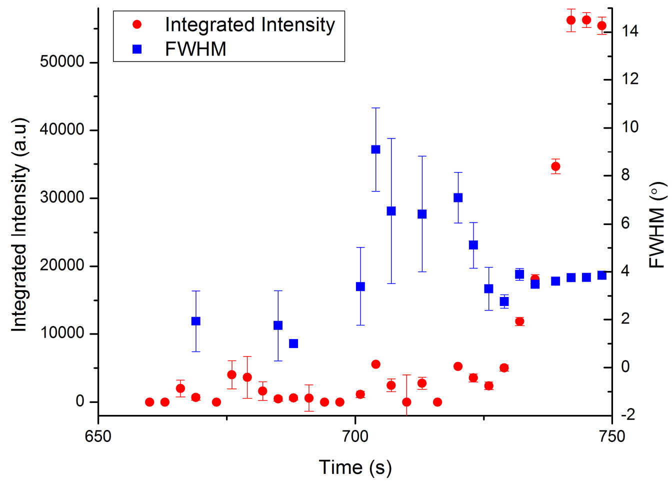




- Weak (111) texture

# Heating rate influences texture

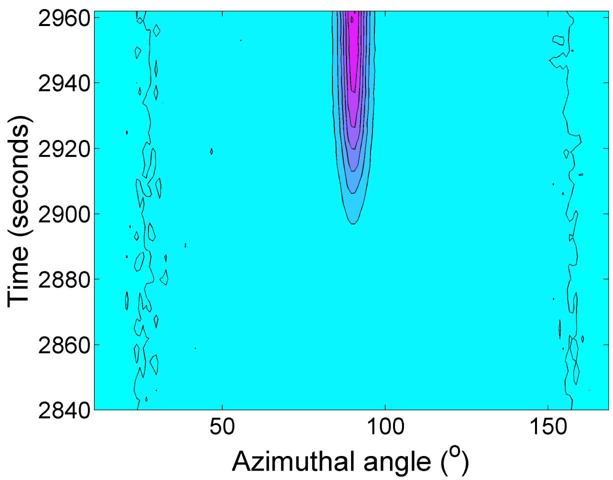
**~1°C/s**

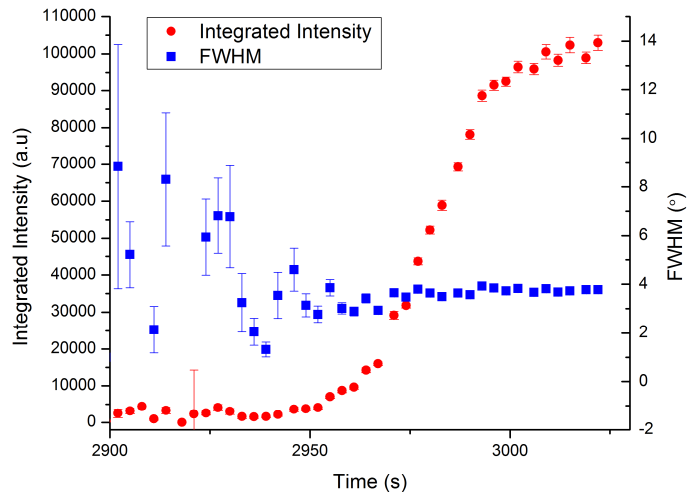



- Mixed texture: weak (111), strong (100),

**~0.5°C/s**

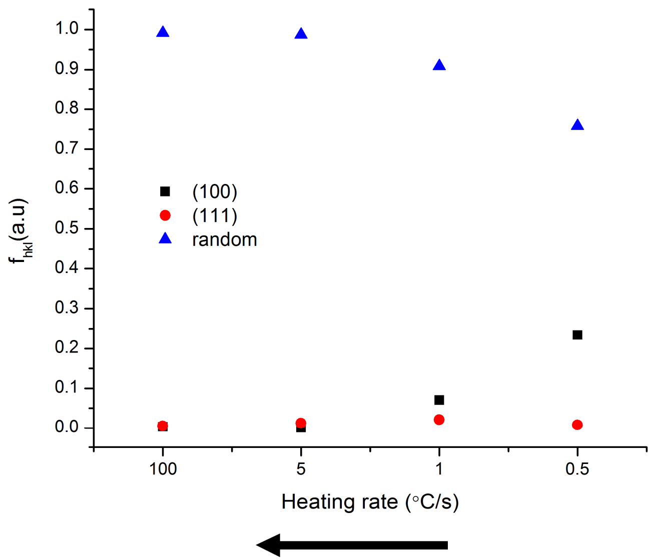


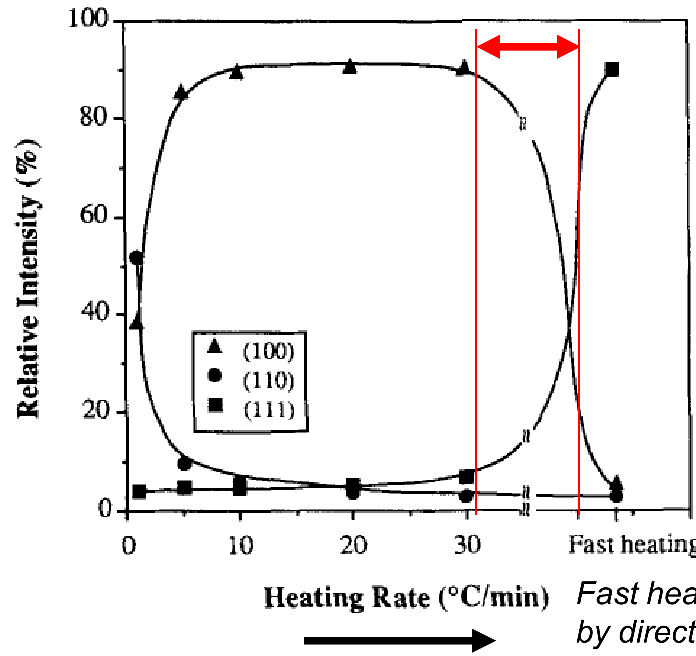




- Strong (100) texture

# Texture consistent with literature*

$$f_{hkl} = \frac{I_{hkl}}{I_{100} + I_{111} + I_{random}}$$



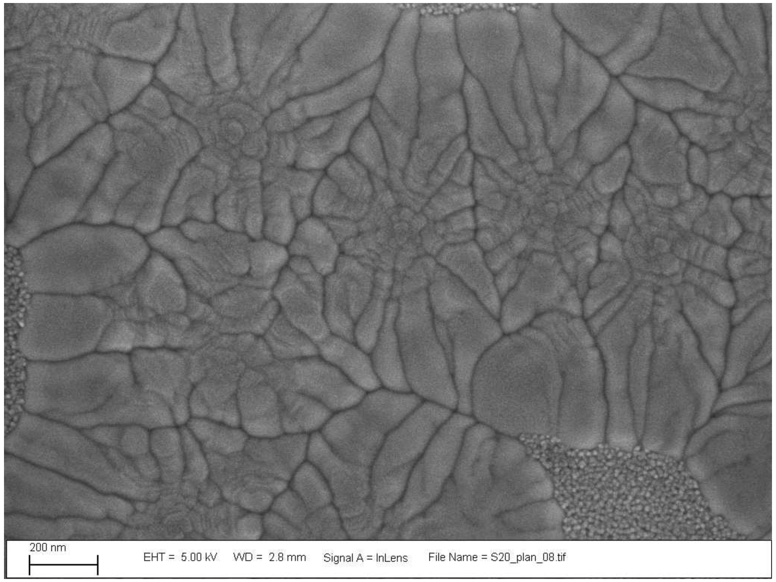

*Fast heating rate achieved by directly placing sample in preheated furnace.*

- (100) texture decreases with increasing heating rate.
- In fast heating rates, homogenous nucleation may dominate over heterogeneous nucleation and growth from the bottom electrode.

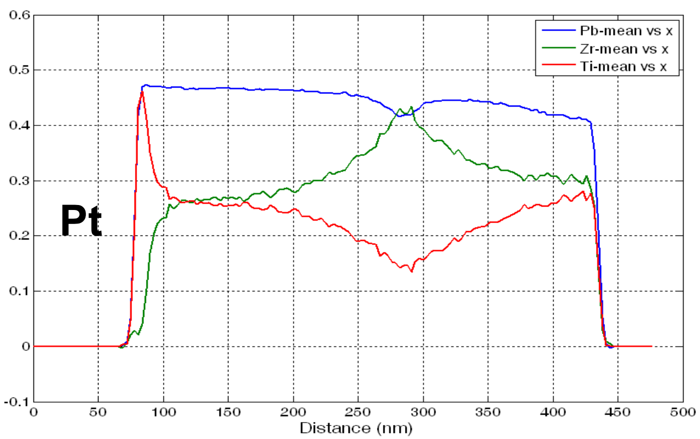
*S. Y. Chen and I. W. Chen, J. Am. Ceram. Soc. 81 (1998) 97.

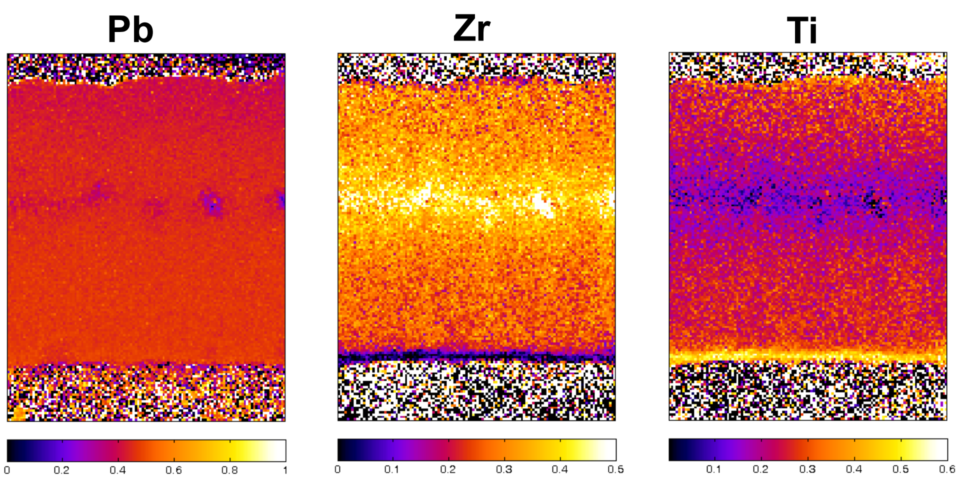
UF UNIVERSITY of FLORIDA

# Microstructure and chemistry

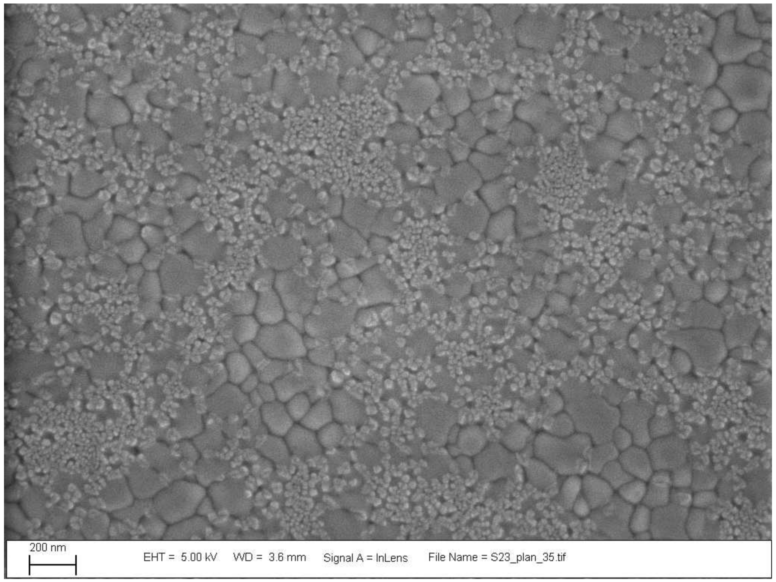



- 100°C/second
- Rosetta-type grain structure
- Porosity observed in the middle of the film
- Some Pb loss at surfaces
- **Ti ($PbTiO_3$?) segregation at interface**

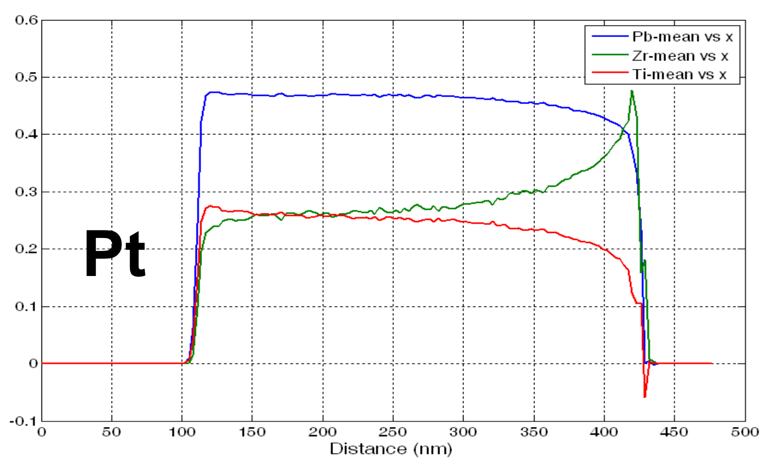


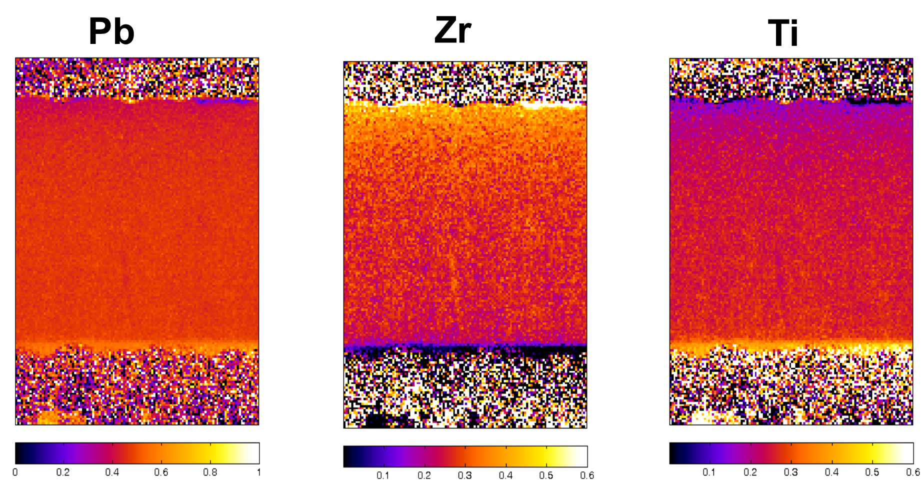



# Microstructure and chemistry

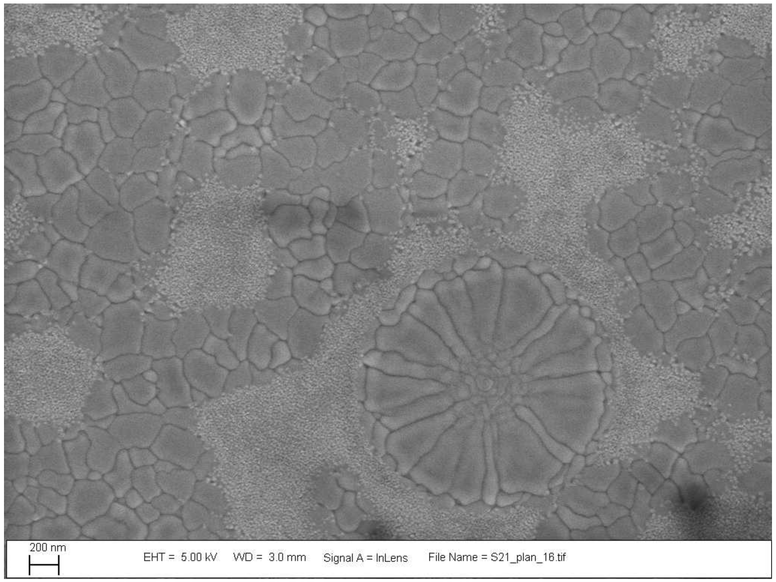



- <u>5°C/second</u>
- Compositional gradient through film
- **Ti preference at interface, less than 50 nm thick**

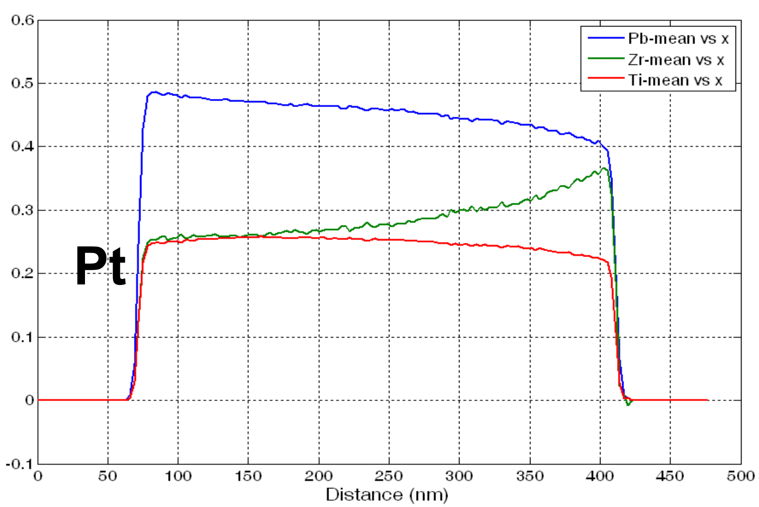


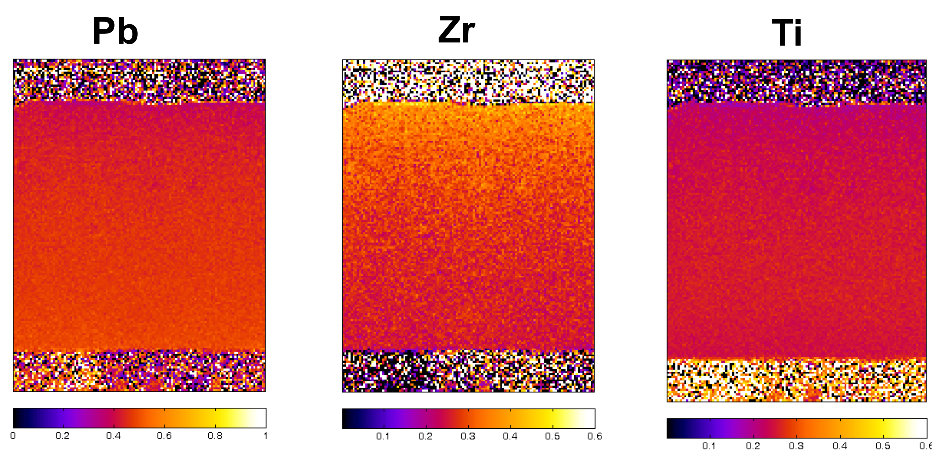



# Microstructure and chemistry

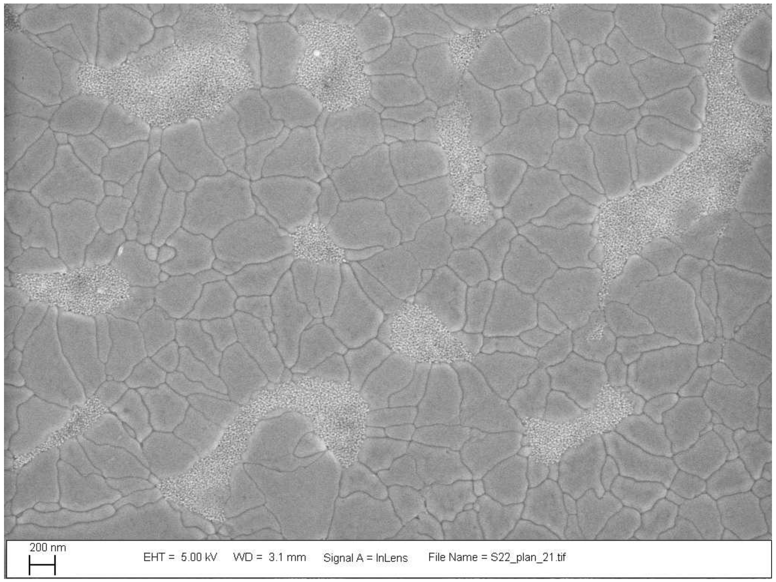



- <u>1°C/second</u>
- No preferential Ti near interface
- Some Zr/Ti segregation through thickness, but less than faster ramp rates.

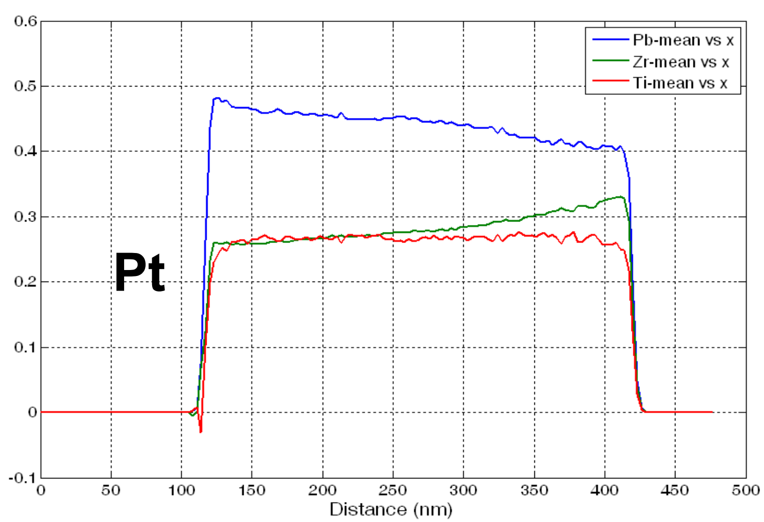


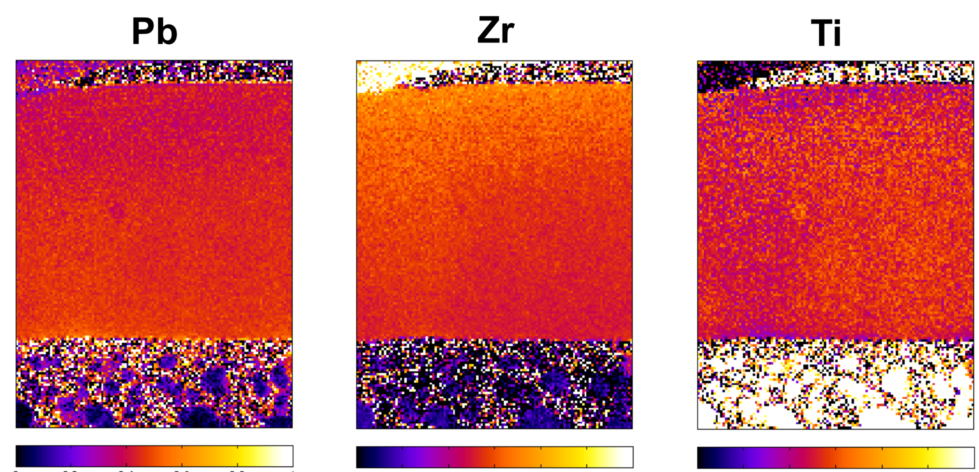



# Microstructure and chemistry



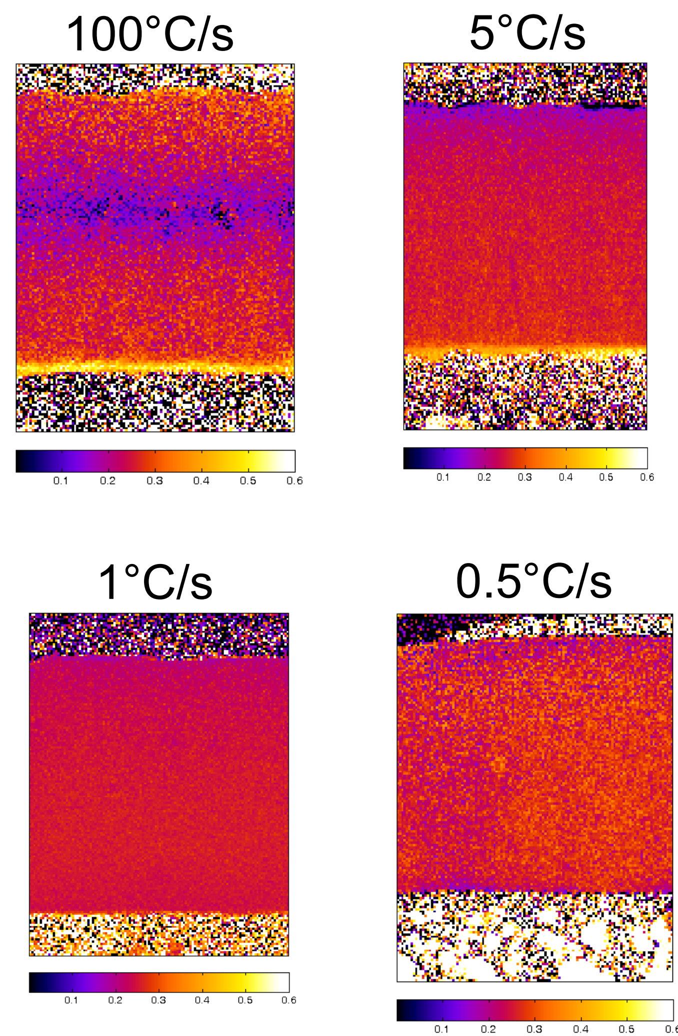

- <u>0.5°C/second</u>
- No preferential Ti near interface
- Some Zr/Ti segregation through thickness, but less than faster ramp rates.



# Origin of Ti segregation at fast heating

Ti maps




Ti-segregation near bottom electrode interface at fast heating rates.

1. $PbTiO_3$-rich nuclei at fast heating rates
   - $PbTiO_3$-rich PZT requires lower energy for nucleation
2. Ti diffusion from adhesion layer at fast heating rates
   - Ti present in Si/Ti/Pt adhesion layer could diffuse to the Pt-film interface to form $TiO_2$

- Both processes need considerable diffusion
- Characterizing Ti across electrode to identify origin of Ti rich layer

F. Calame and P. Muralt, Applied Physics Letters 90 (2007).
P. Muralt et al., J. Appl. Phys. 83 (1998) 3835.

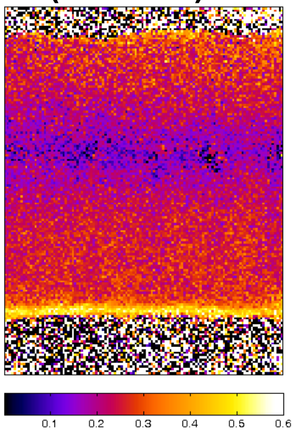
# Summary and Conclusions

- Laboratory and synchrotron based in situ X-ray diffraction methods were developed to characterize phase and texture evolution in PZT thin films
- $Pt_xPb$ observed to form preferentially during fast heating rates, perhaps due to concentration of Pb at film-Pt interface
- $Pt_xPb$ might not directly nucleate (111) texture in solution deposited PZT thin films
  - PtxPb are not coincident in time (separated by fluorite)
  - Lattice matching may only be correlation

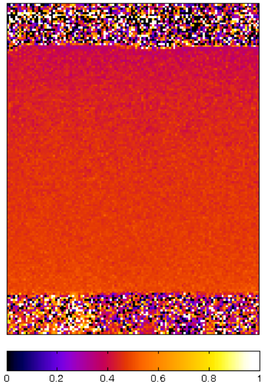
# Summary and Conclusions

- Fast heating rates leads to Ti segregation at the interface, perhaps correlated with $PbTiO_3$ nuclei
- Fast heating rates reduces the (100) texture strength, likely due to competing heterogeneous nucleation
- Pb loss at surfaces is apparent, most notably at slow heating rates

Ti (100°C/s)




Pb (1°C/s)



# Phase and texture evolution in solution deposited PZT thin films during slow and fast heating rates

*Nittala*

Jacob L. Jones[1], Krishna Nittala[1],
Geoff L. Brennecka[2], Jon F. Ihlefeld[2], Bruce A. Tuttle[2], and
Douglas S. Robinson[3]

*[1]Department of Materials Science and Engineering, University of Florida, Gainesville, FL, USA*
*[2]Sandia National Laboratories, Albuquerque, NM, USA*
*[3]Advanced Photon Source, Argonne National Laboratory, Argonne, IL, USA*

1 UF UNIVERSITY of FLORIDA College of Engineering

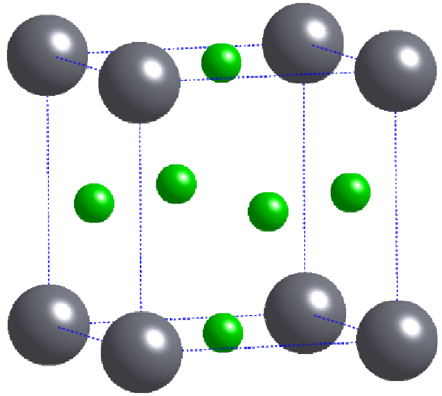
2 Sandia National Laboratories

3 Argonne NATIONAL LABORATORY

***Support**: Supported by the National Institute for NanoEngineering (NINE) and the Laboratory Directed Research and Development (LDRD) program at Sandia National Laboratories.*

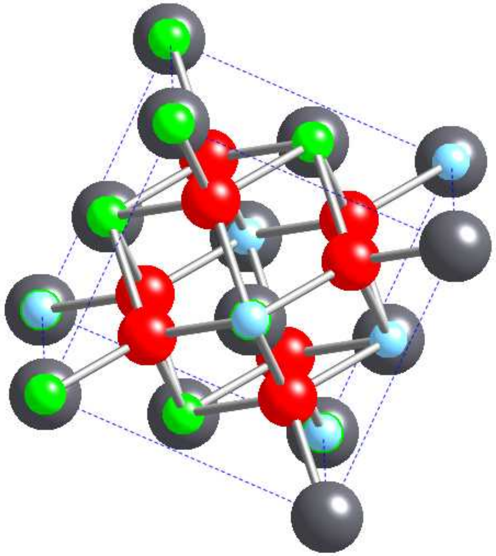
# Intermediate phases

- $Pt_xPb$: formed due to the highly reducing conditions at the film - Pt electrode interface.



$Pt_xPb$

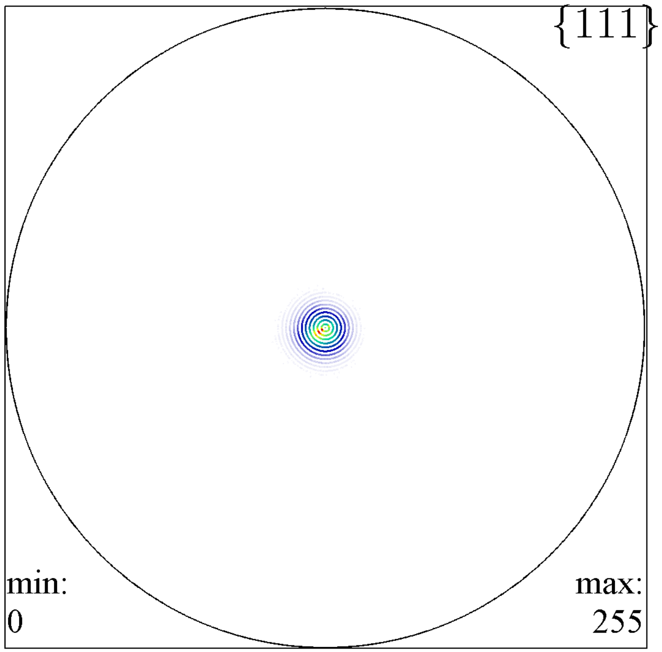
- Relative stability of fluorite effected by dopant additions.[5]

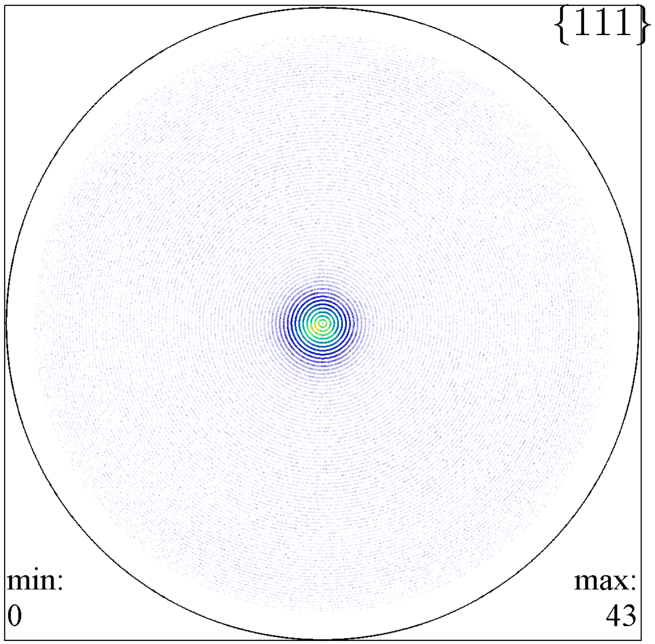


Fluorite

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

# $Pt_xPb$: Pole Figures

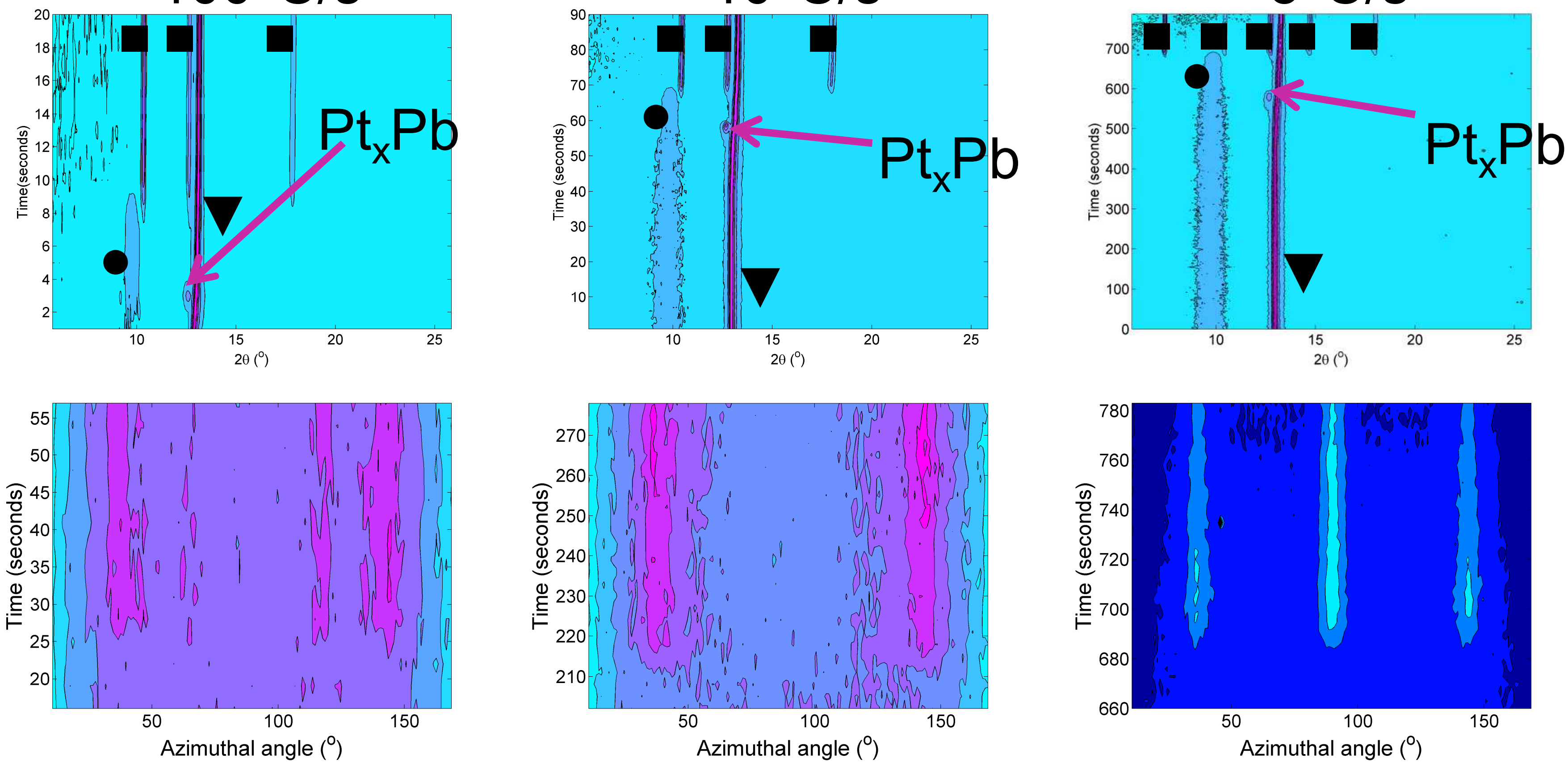



- Pt
- $Pt_xPb$

# PNZT

~100°C/s ~10°C/s ~5°C/s



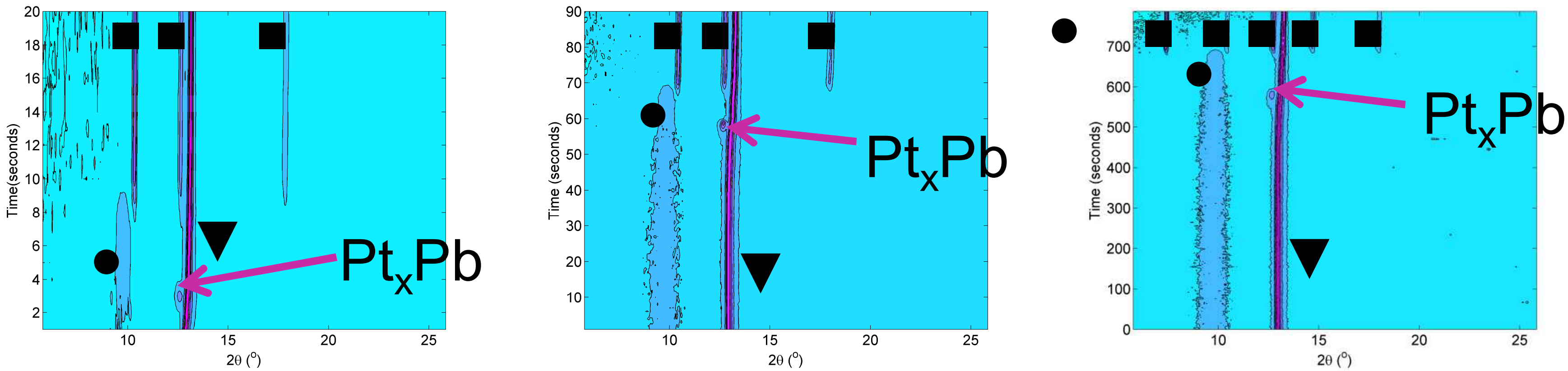

Random texture; small (111) texture ▼

(111) texture ■

Mixed (111) + (100) texture ●

# PNZT

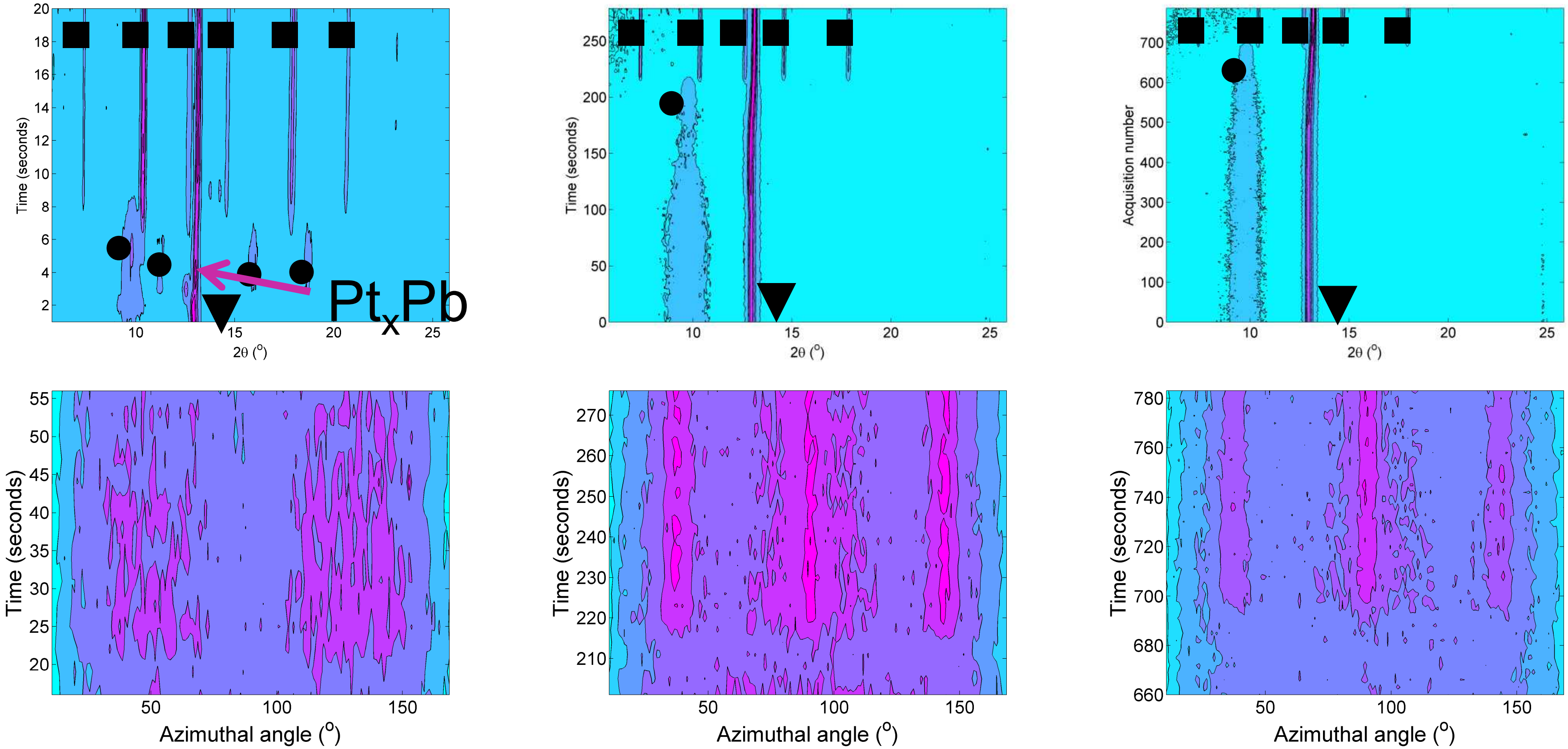
~100°C/s ~10°C/s ~5°C/s




- Phase and texture evolution is observed to be similar to PZT.
- Pt$_x$Pb is observed for all heating rates; similar to PZT.

# PLZT

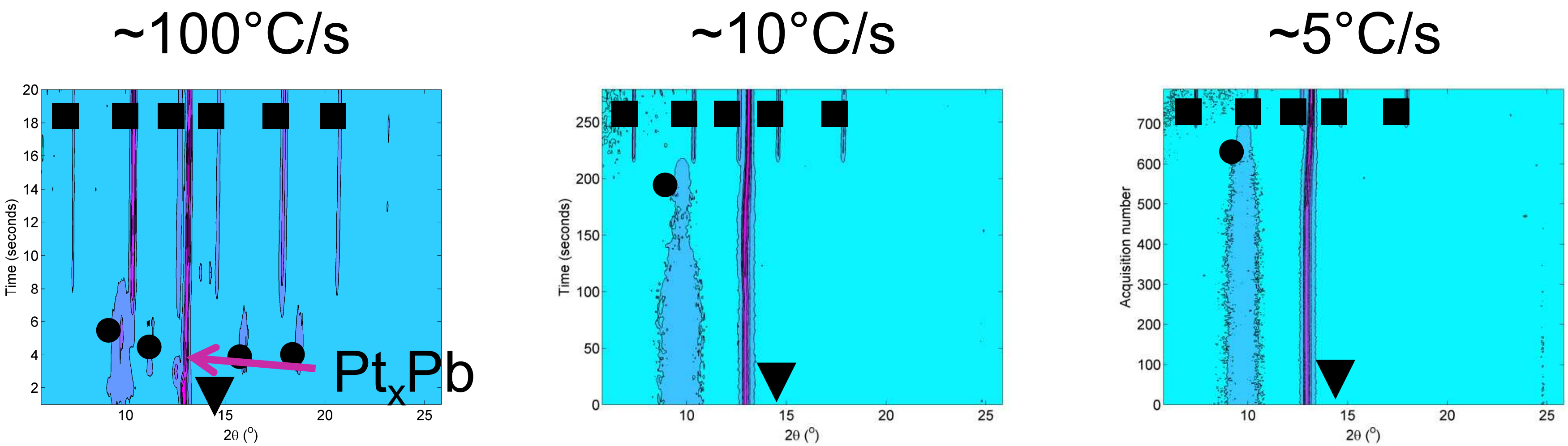
| ~100°C/s | ~10°C/s | ~5°C/s |
|---|---|---|




| Random texture | Mixed (111) + (100) texture | Mixed (111) + (100) texture |
|---|---|---|

▼ ■ ●

# PLZT

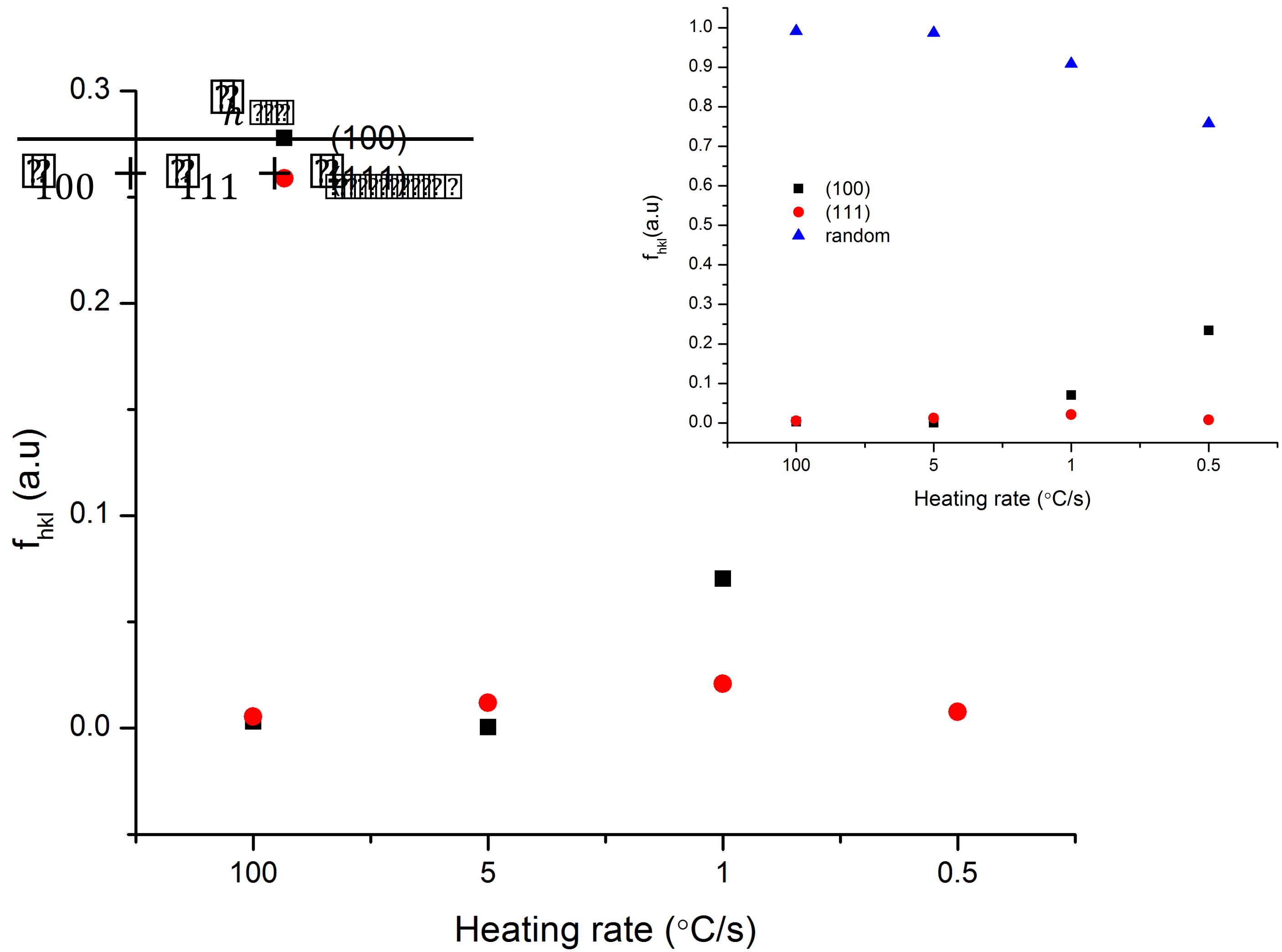



- $Pt_xPb$ is observed only for the fastest heating rate.
- The variation of texture with heating rate is observed to be similar to PNZT and PZT.
- Lanthanum doping could be effecting $Pt_xPb$ stability during crystallization.

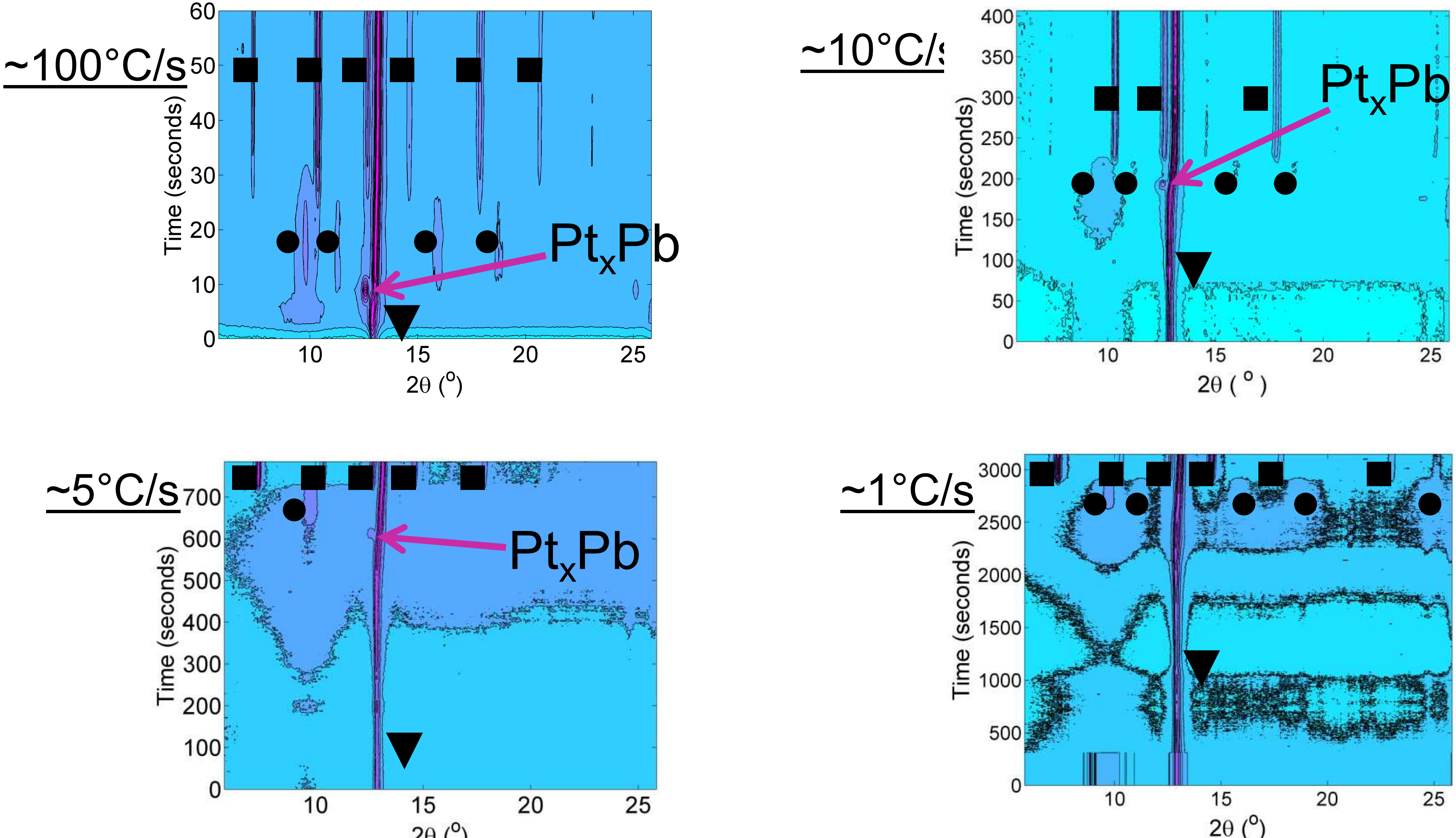
▼ ■ ● texture texture

# Variation of texture with heating rate

$$?_{h??} = \frac{?_{h??}}{?_{100} + ?_{111} + ?_{???????}}$$

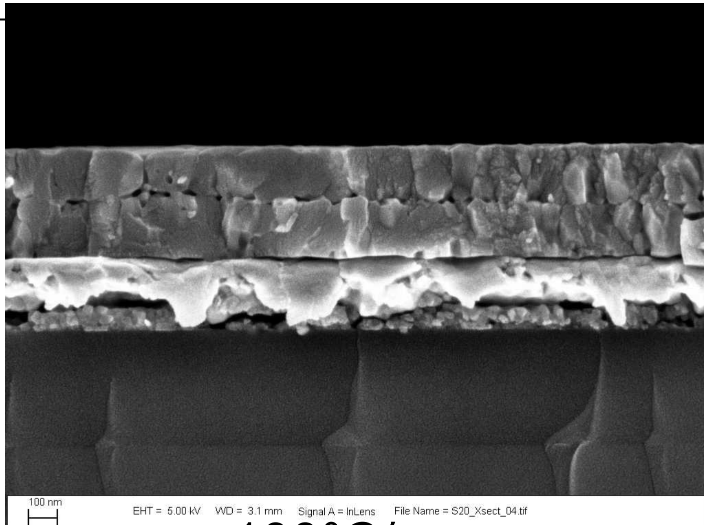


# No overlap between $Pt_xPb$ and Perovskite

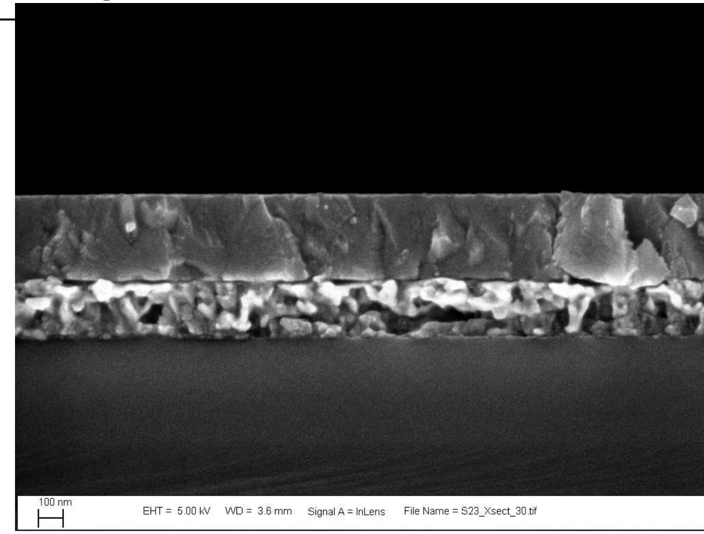



▼ Pt ■ Perovskite ● Fluorite

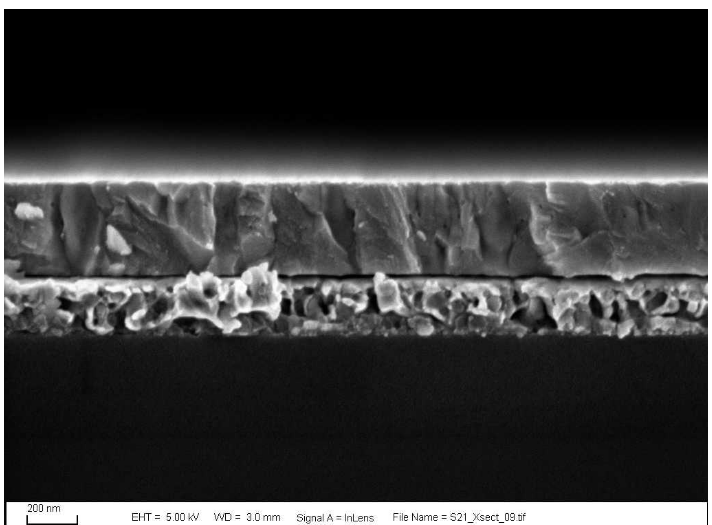
# Elevation views of crystallized films



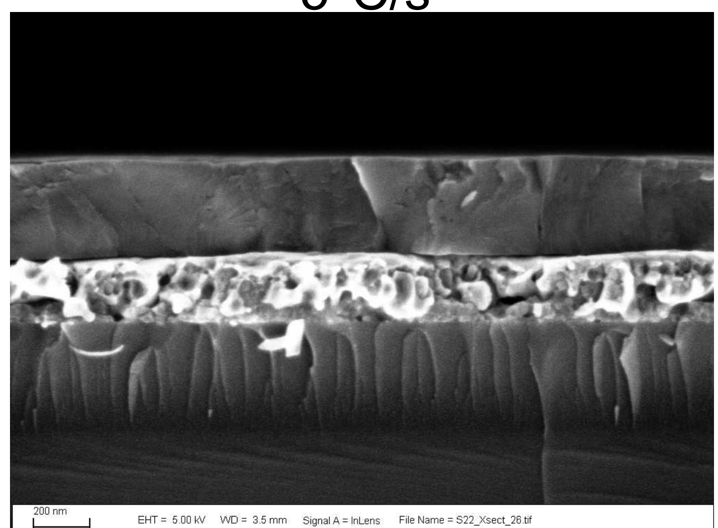

~100°C/s




~5°C/s

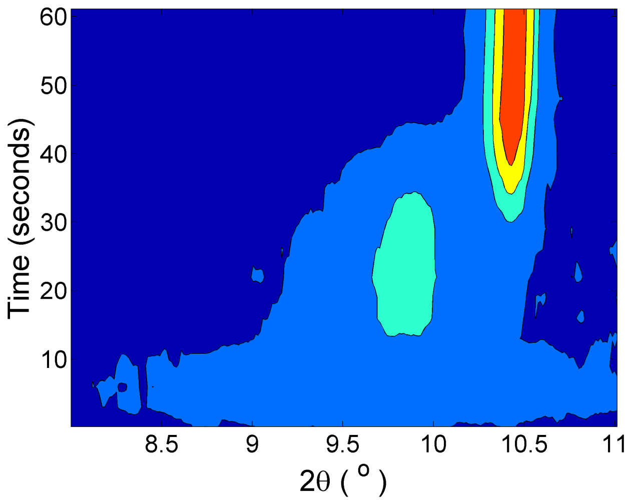


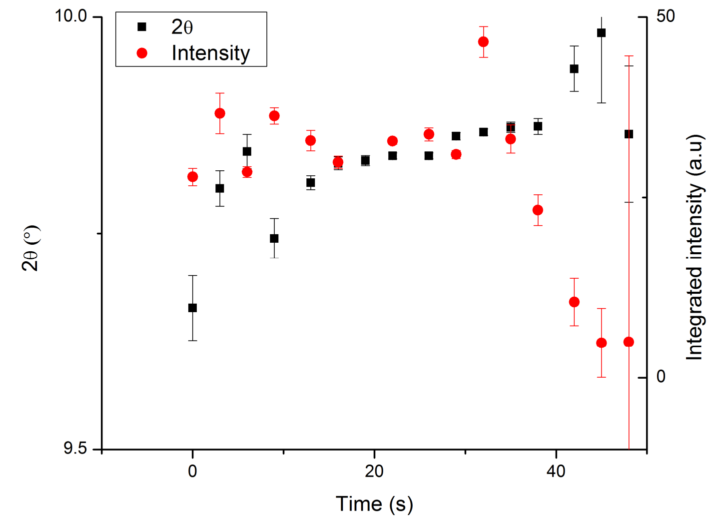

~1°C/s



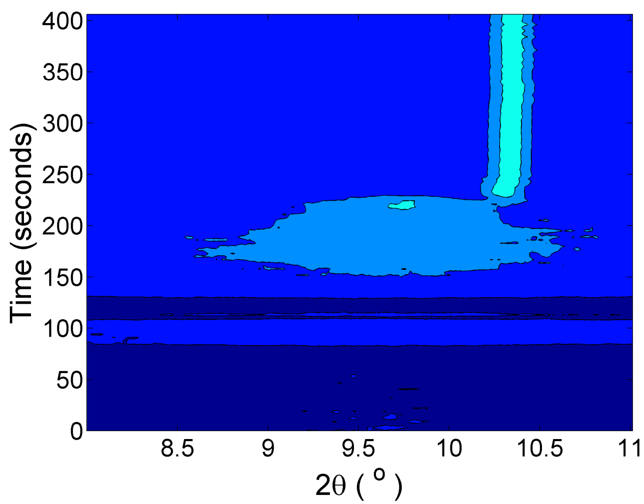

~0.5°C/s

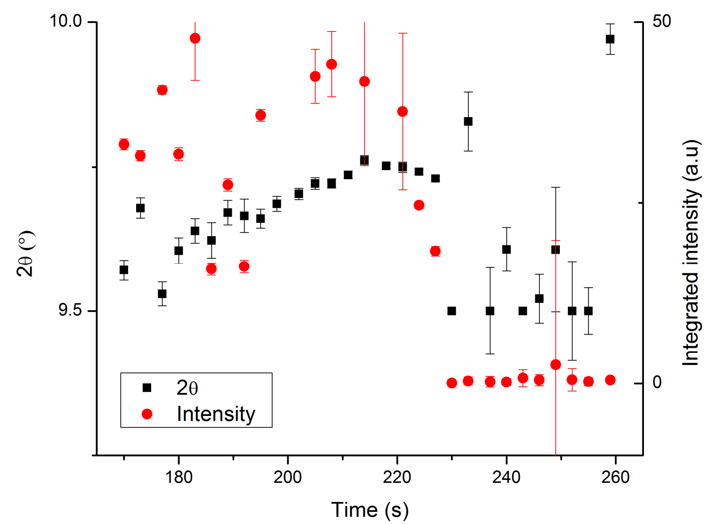
# Evolution of Fluorite phase: Intensities



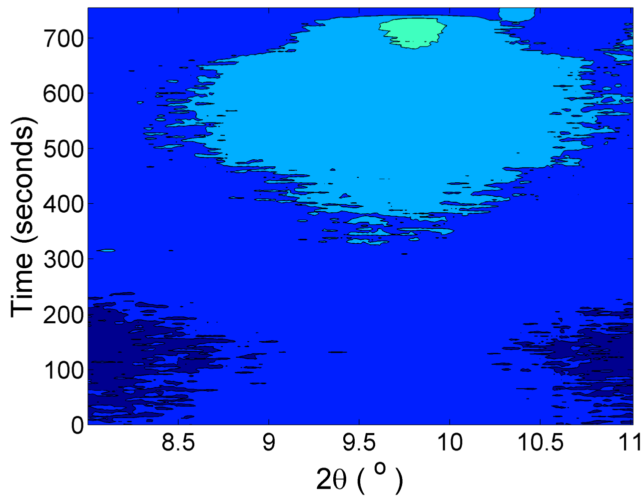

100 °C/s

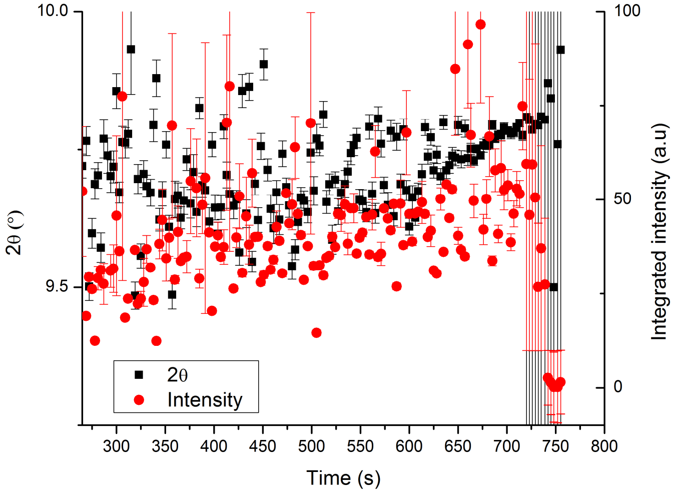


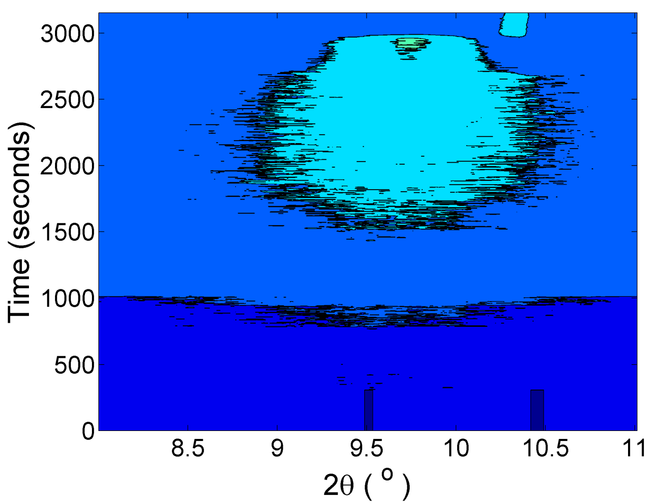

5 °C/s

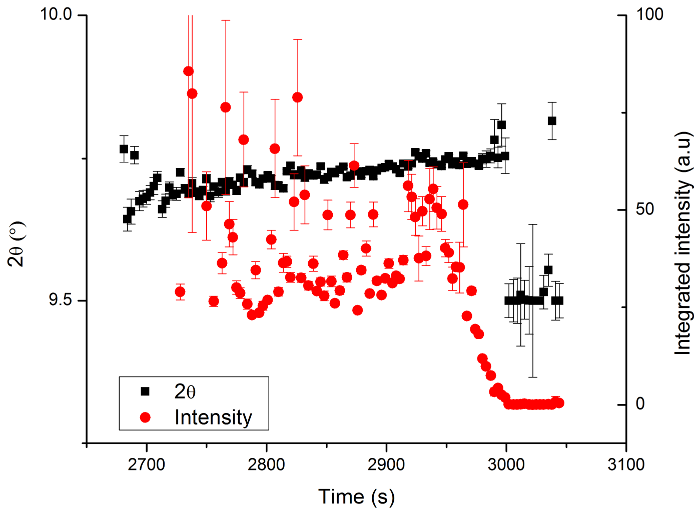
# Evolution of fluorite phase: Intensities




1 °C/s



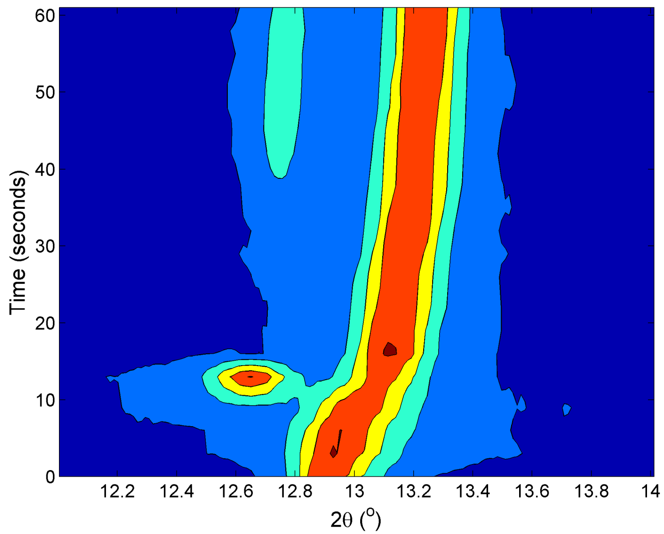




0.5 °C/s

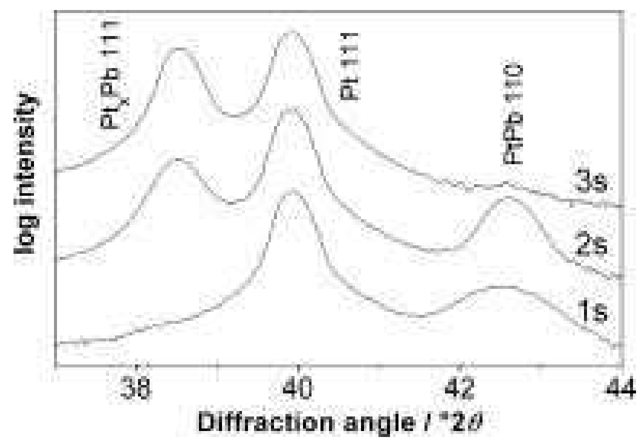
- For Discussion

# PtPb and $Pt_xPb$ phases

- A PtPb type phase was observed to form in addition to $Pt_xPb$ by Dippel et al.
- A slight shoulder is observed to the right of the Pt peak before $Pt_xPb$ formation
- This shoulder could be due to the PtPb phase



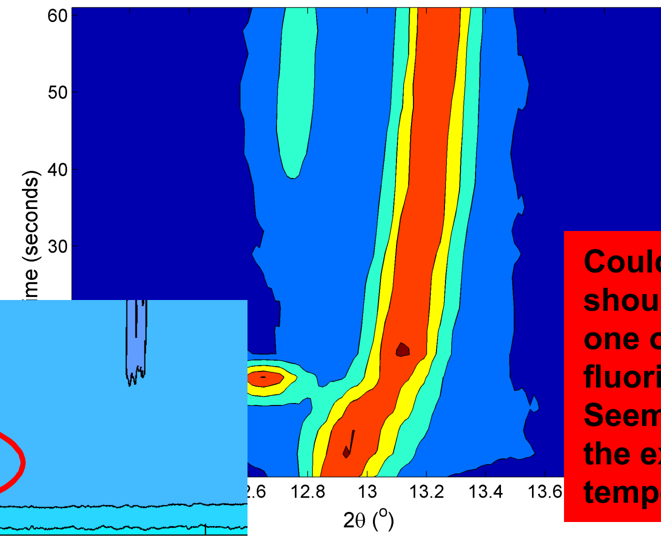

1 °C/s



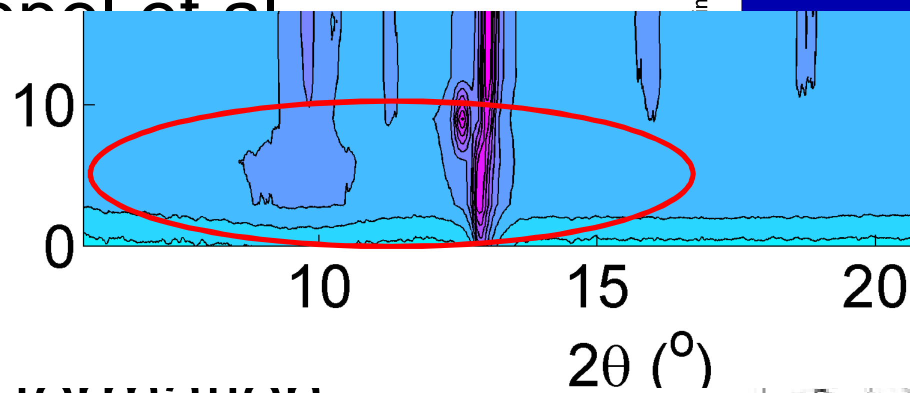

Dippel et al Chem. Mater. (2010).

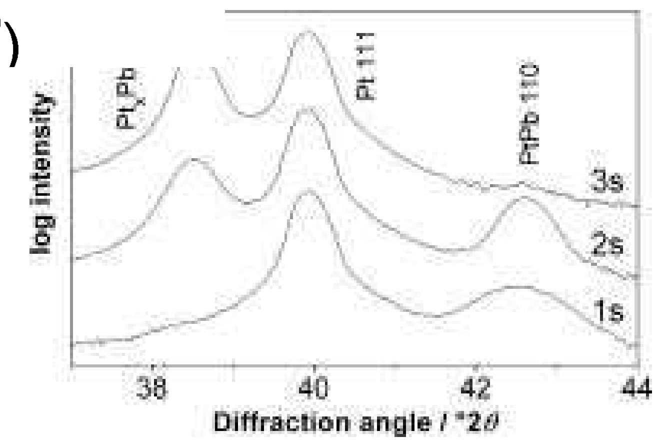
# PtPb and $Pt_xPb$ phases

- A PtPb type phase was observed to form in addition to $Pt_xPb$ by Dippel et al.
- A sl obs of th $Pt_xPb$ formation
- This shoulder could be due to the PtPb phase




Could this shoulder also be one of the fluorite peaks? Seems to form at the exact same temperature.



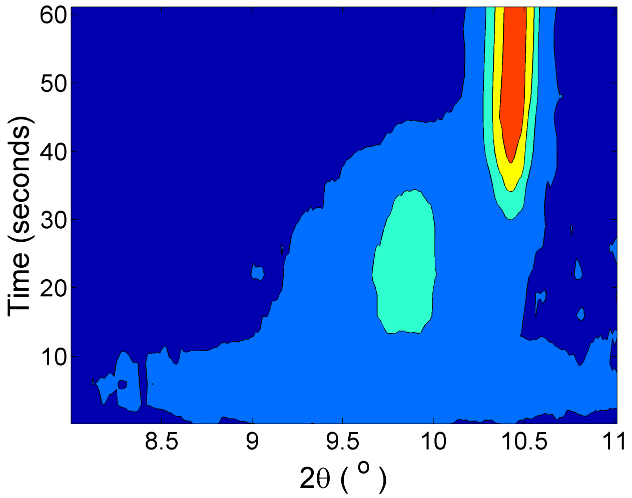



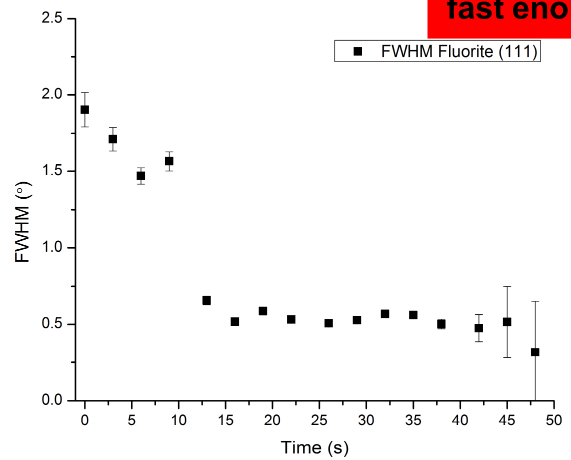

Dippel et al Chem. Mater. (2010).

# Evolution of Fluorit

You have more temperature steps in the slower heating rates. So perhaps you are just missing the transition in the faster heating rate because we cannot measure fast enough.

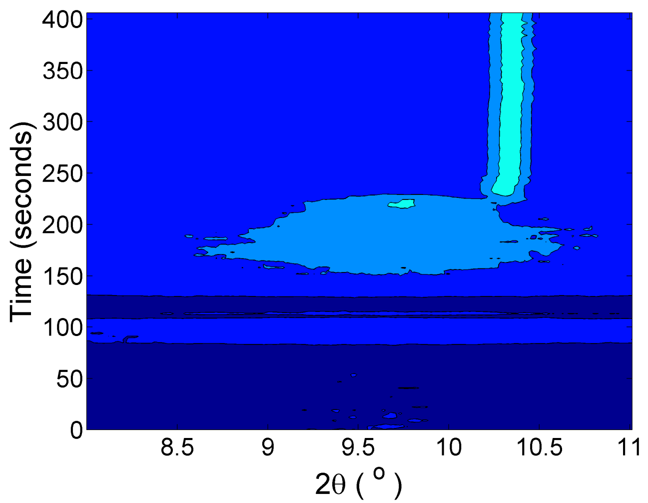
100 °C/s

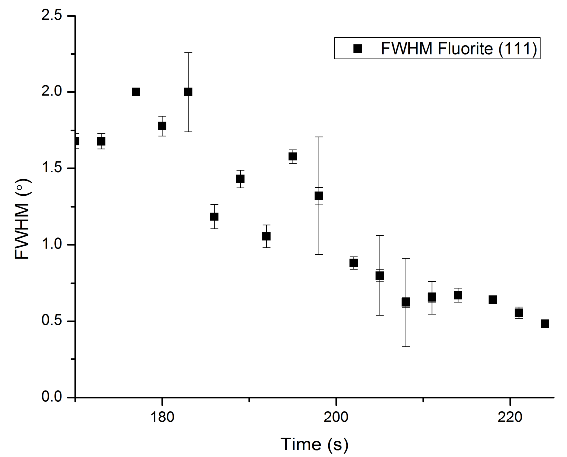



- Amorphous phase transforms to fluorite phase
- FWHM shows instantaneous change

5 °C/s

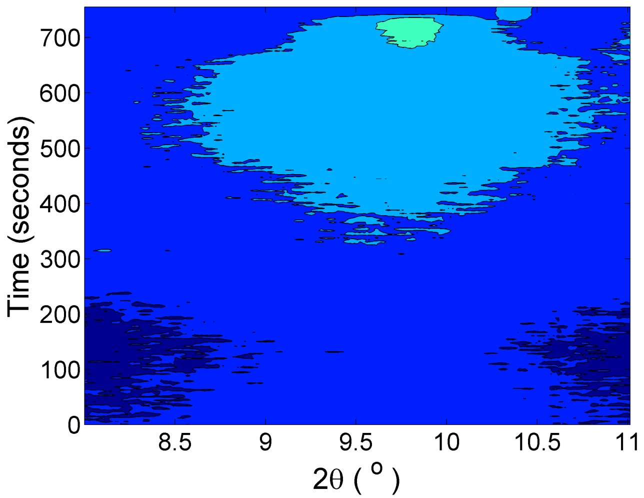


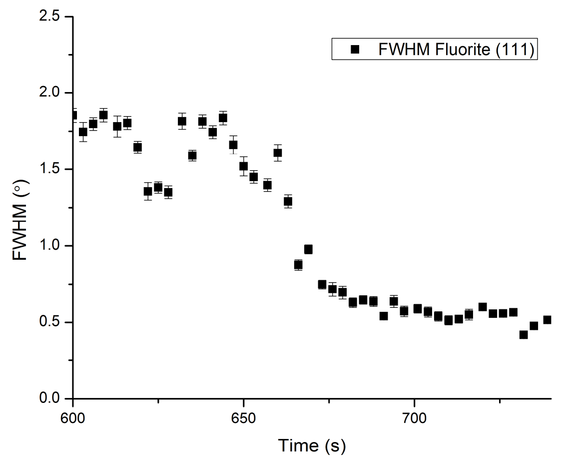




- FWHM observed to gradually change with time for slower heating rates

# Evolution of Fluorite phase (cont)

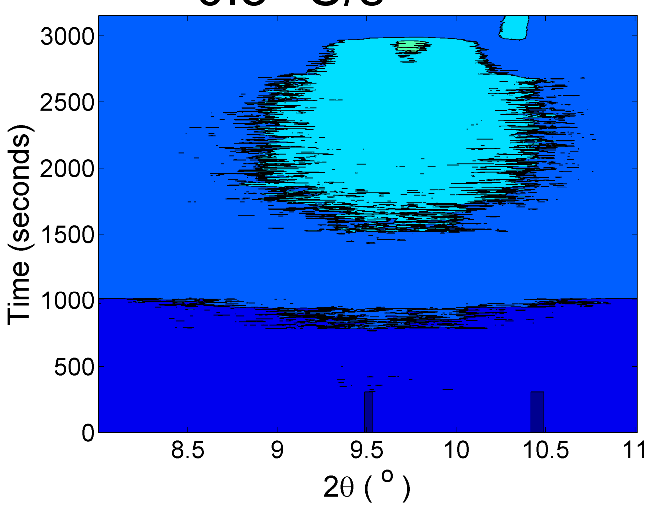
1 °C/s

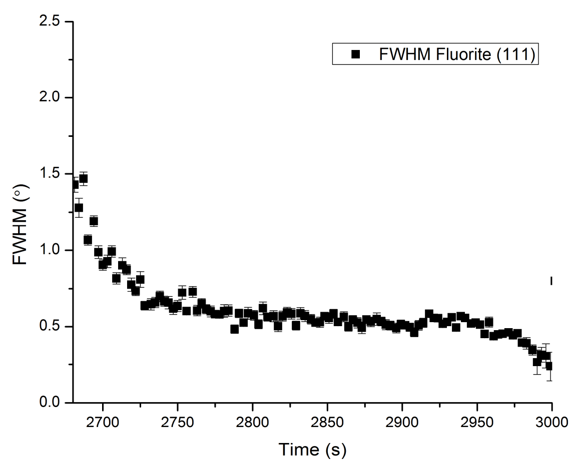



- FWHM gradually with time

0.5 °C/s

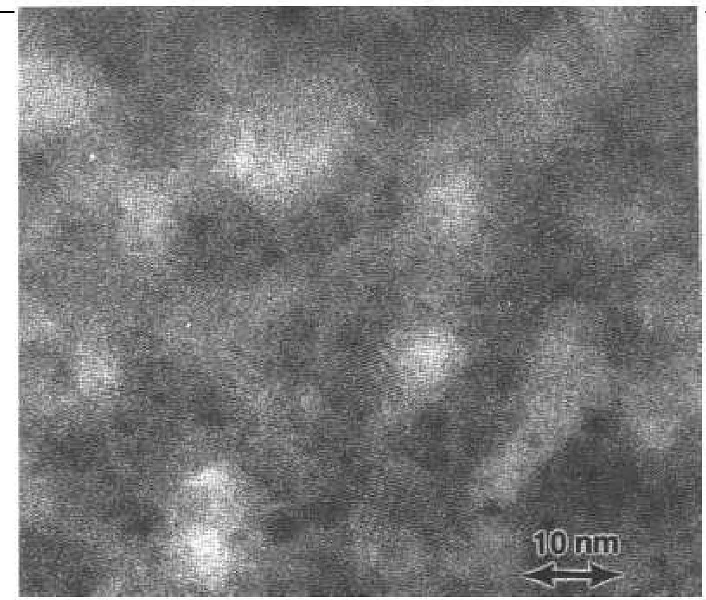



- FWHM gradually with time

# Evolution of Fluorite phase

- The transformation of the amorphous hump to the fluorite phase seems to be continuous
- Suggesting that nanoscale fluorite phase formed during pyrolysis could transfrom into the final fluorite phase




B. A. Tuttle et al. J. Mater. Res. (1992)

Nanoscale regions fluorite type phase formed after ...olysis

What is the significance of this? This seems obvious to me. But perhaps I don't understand what you mean.