SAND2007-3456C

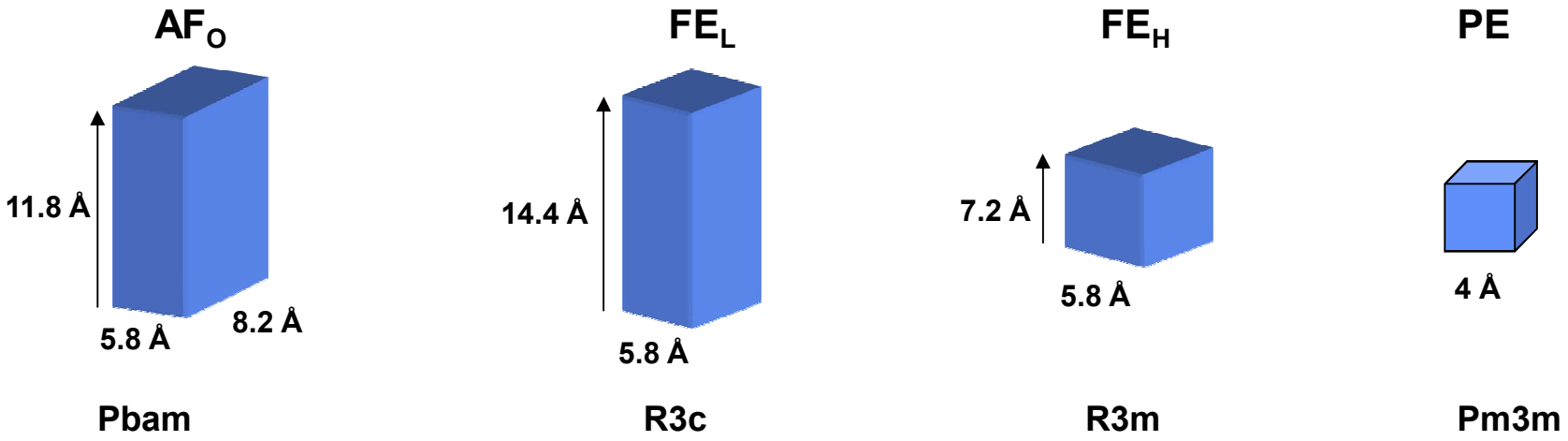
X-Ray and Neutron Diffraction Analysis of Nb-Doped and Undoped PZT 95/5

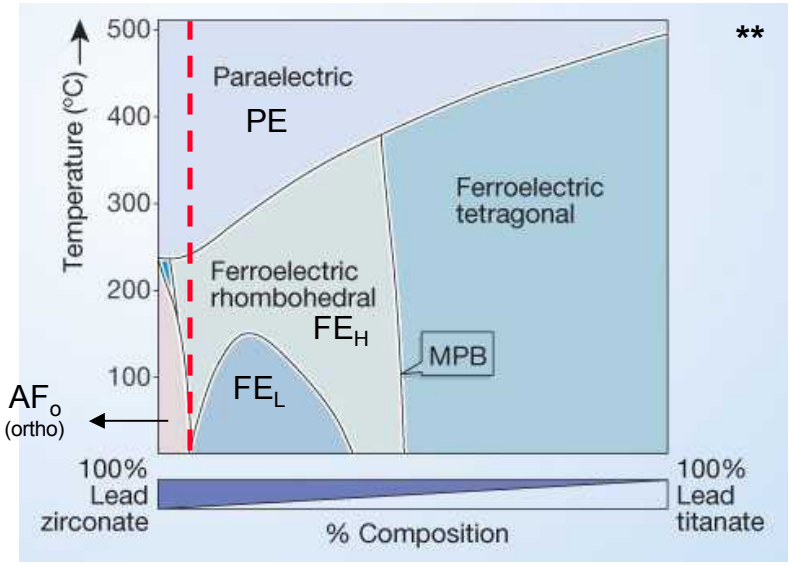
Mark A. Rodriguez, Colleen S. Frazer, Pin Yang
Sandia National Laboratories
Albuquerque, NM

Sven C. Vogel
Los Alamos National Laboratory
Los Alamos, NM

The 8th LANSCE User Group Meeting
Santa Fe, NM June 12, 2007

The perovskite lattice in the Zr-rich region of $Pb(Zr,Ti)O_3$ (i.e. PZT) contains many phase transitions.



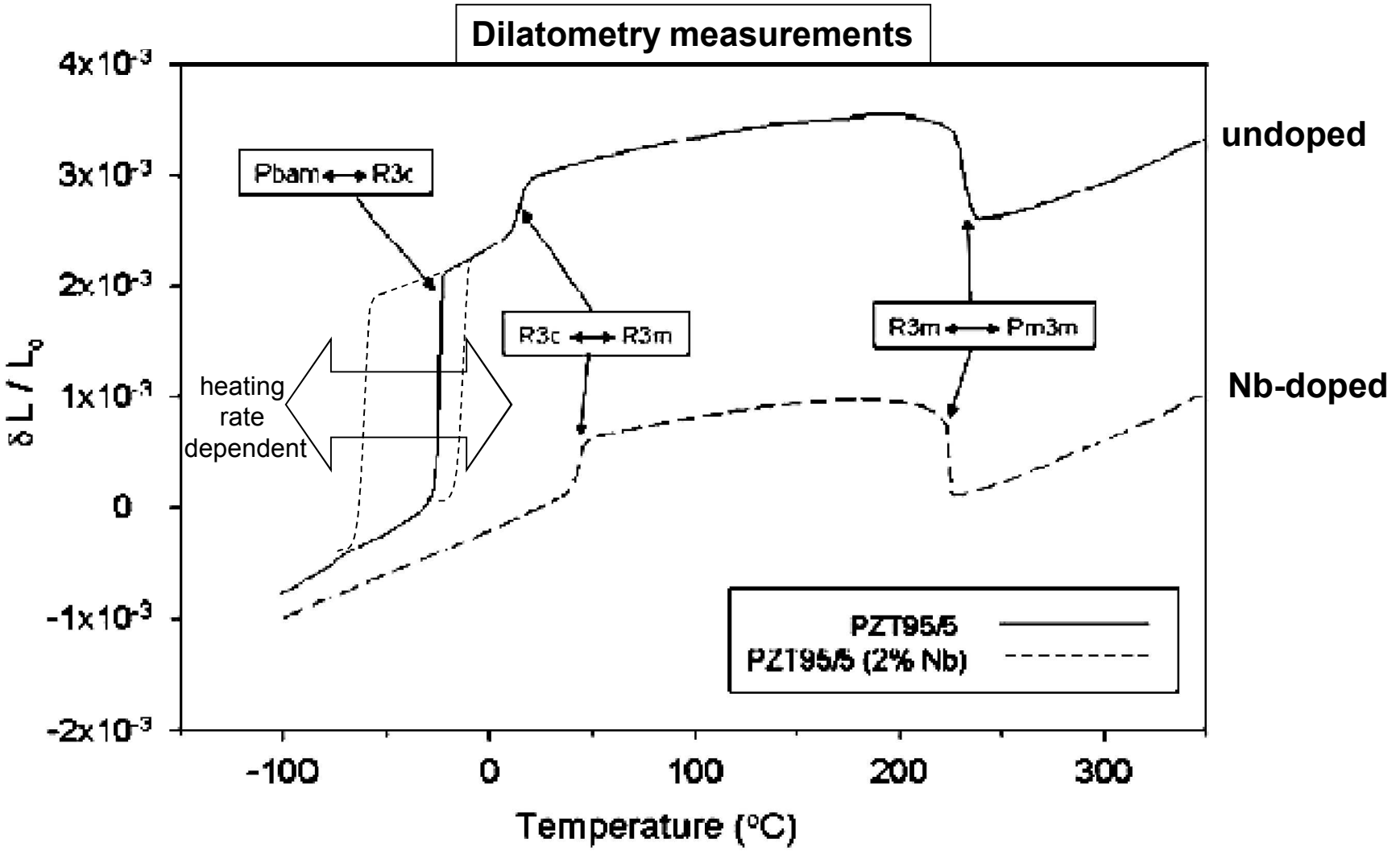


The phase transition from the Ferroelectric rhombohedral phase to the Anti-ferroelectric (AF_O) results in the loss of ferroelectric properties for PZT 95/5

*Noheda, B., Gonzalo, J.A., and M. Hagen. "Pulsed Neutron Diffraction Study of Zr-Rich PZT", *J. Phys: Condens. Matter* **11** (1999) 3959-3965.; ** Nature, 03142-f2.2; Viehland, et. al. , *J. Phys. Chem. Solids*, **57,** 1545 (1996).

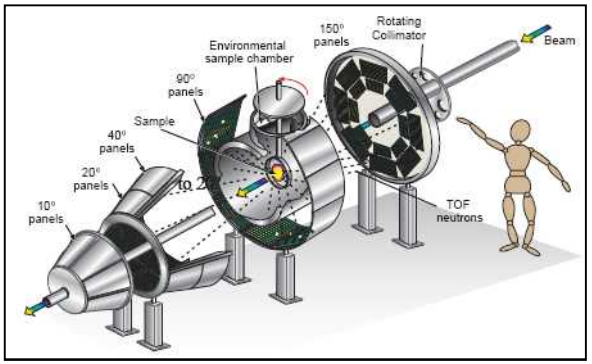
Dilatometry measurements of undoped PZT-95/5 show a dramatic phase transition at low temperature.

Nb-doped PZT-95/5 composition shows no such transition.



We wanted to investigate the structure of Nb-doped and undoped PZT 95/5 as a function of temperature.

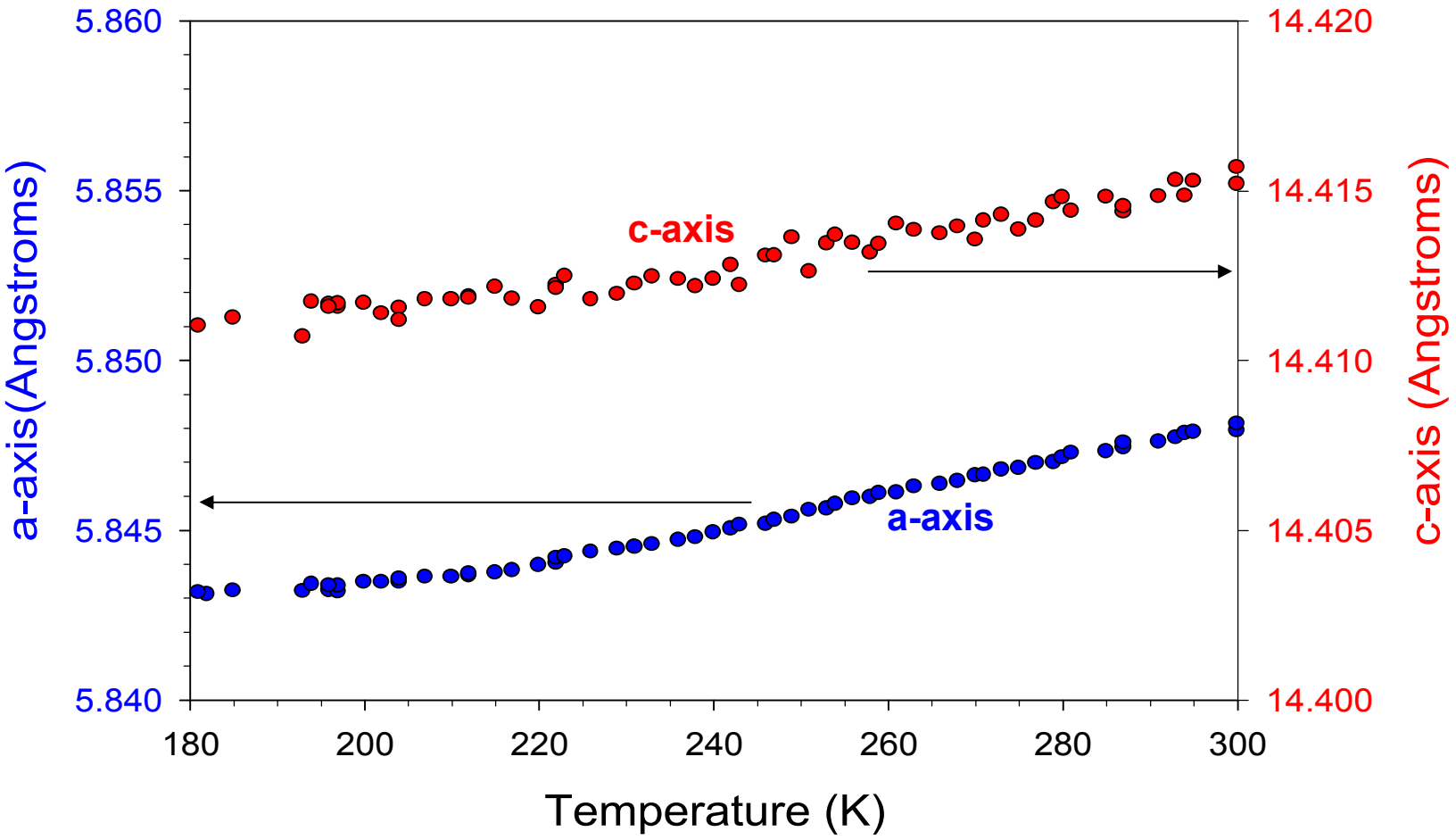
- What structural changes occur as a function of temperature?
- What are the subtle differences between Nb-doped and undoped structures?
- We used the HIPPO neutron spectrometer at LANSCE to collect neutron diffraction data for PZT as a fn(T).



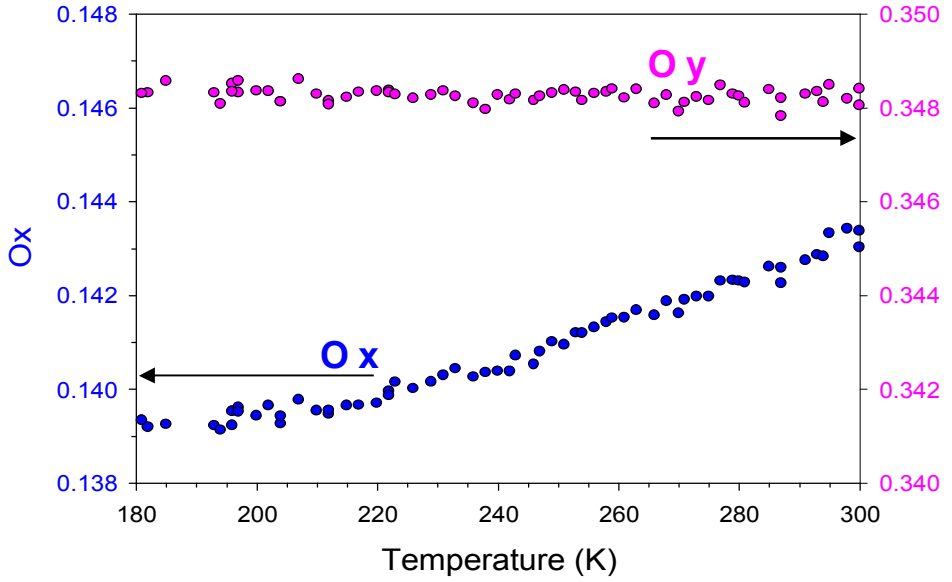
Schematic
Of HIPPO

Sandia National Laboratories

Lattice parameters for Nb-doped PZT 95/5 show no surprises. Structure is R3c (FE_L) from 180 K to 300 K.

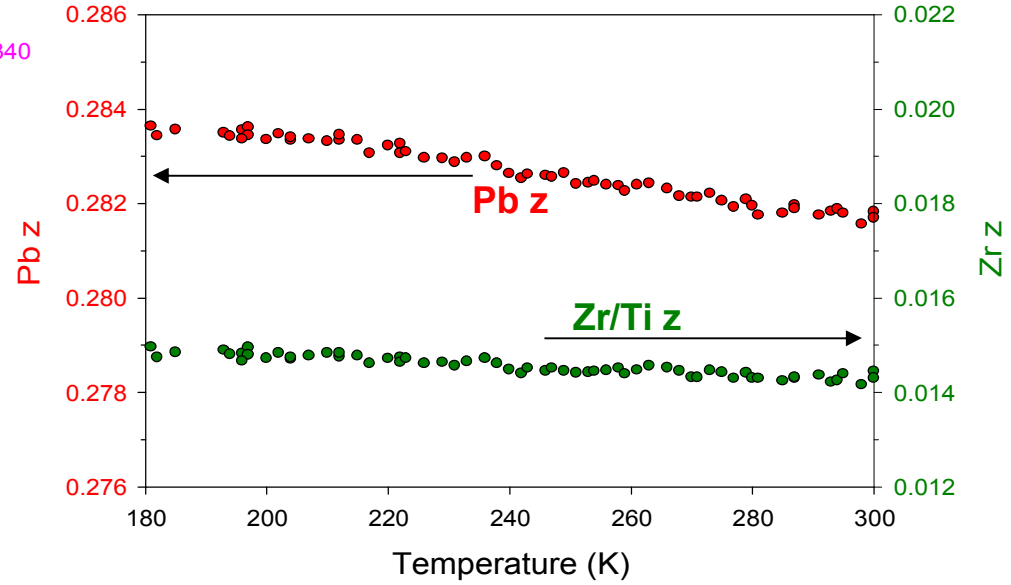


Atom positions for Nb-doped PZT 95/5 show no surprises either. Structure refines well as R3c (FE_L) from 180 K to 300 K.



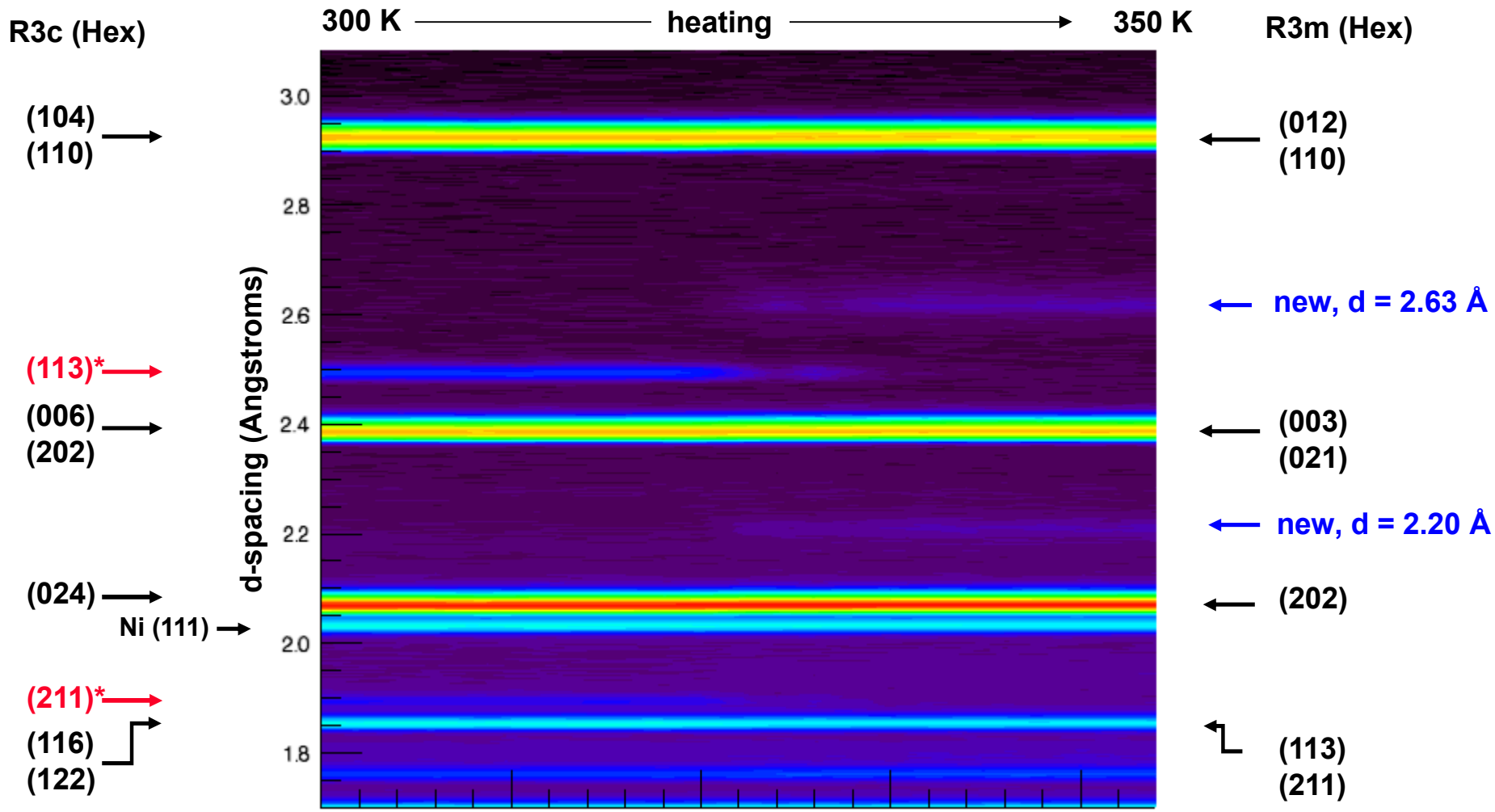
Oxygen site:
(x, y, 0.0833)

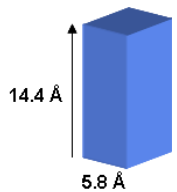
Pb and Zr sites:
(0, 0, z)



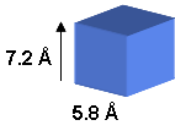
Sandia National Laboratories

A surprise: Nb-doped PZT 95/5 shows some new peaks when heated through R3c-R3m transition.



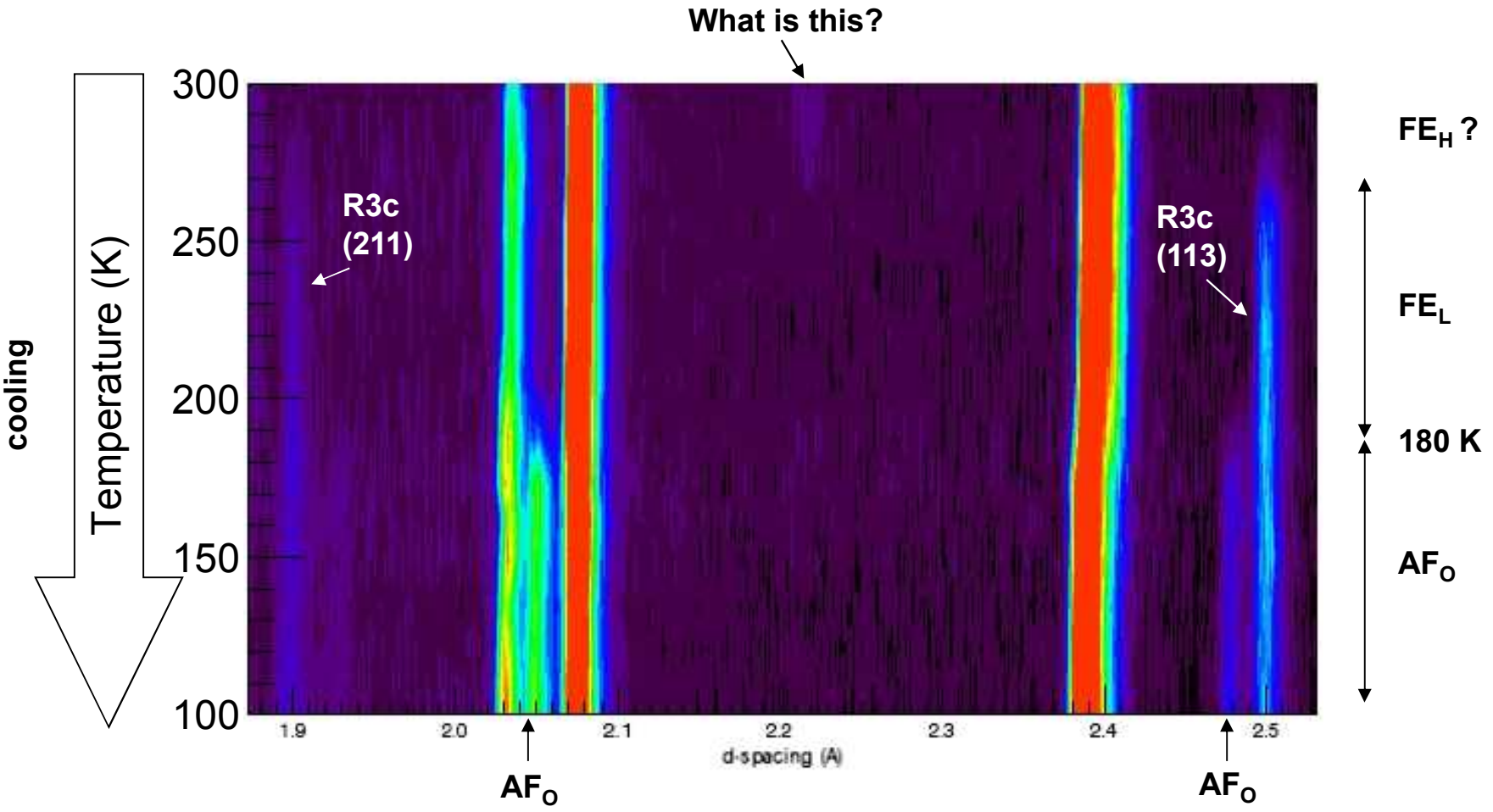


* These peaks become extinct in R3m cell



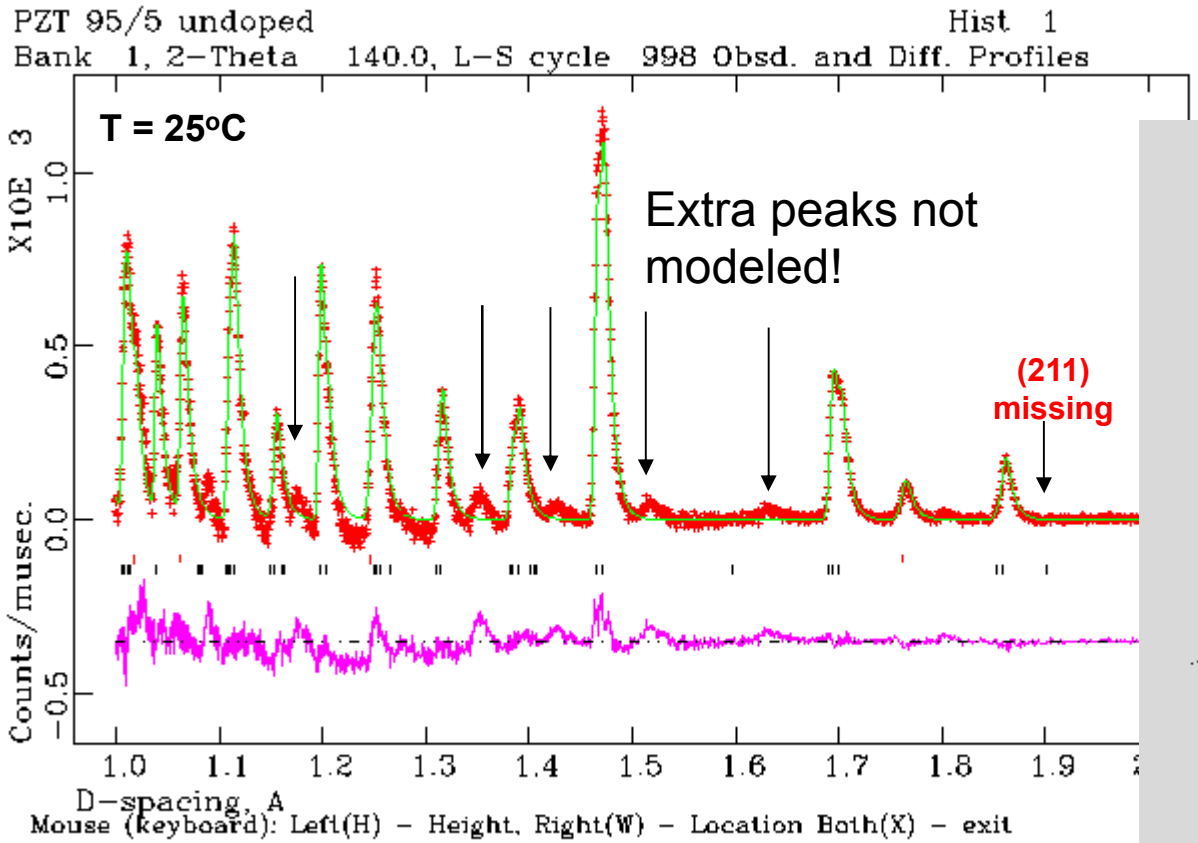
Sandia National Laboratories

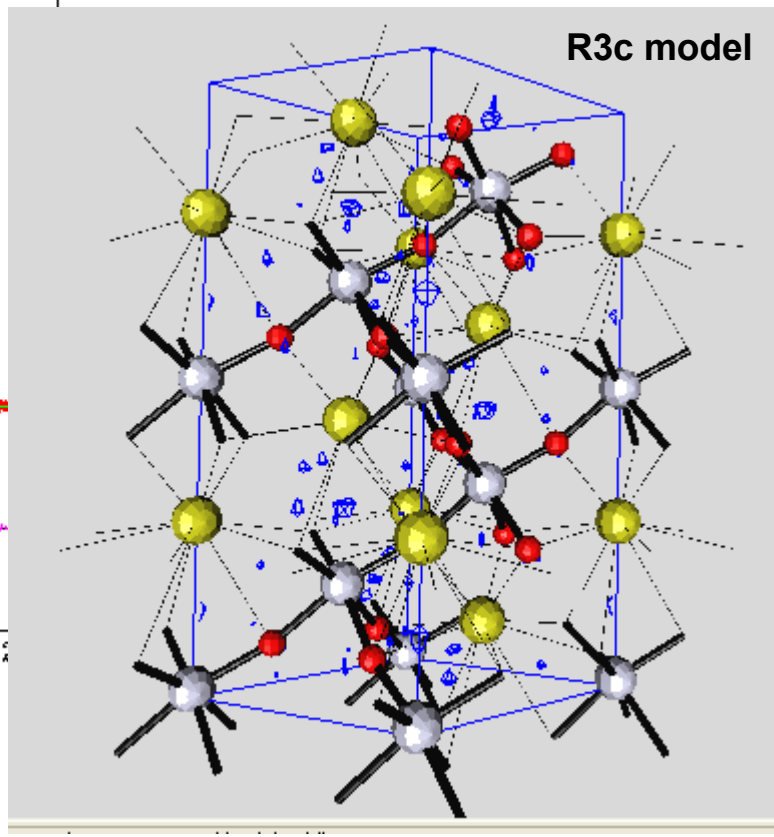
Cooling of Undoped PZT 95/5 shows a dramatic transition to the AF_O phase ~180 K.



A refinement of undoped PZT 95/5 (T = 300 K) shows extra peaks that do not index as R3c or R3m.

Where are these extra peaks coming from?



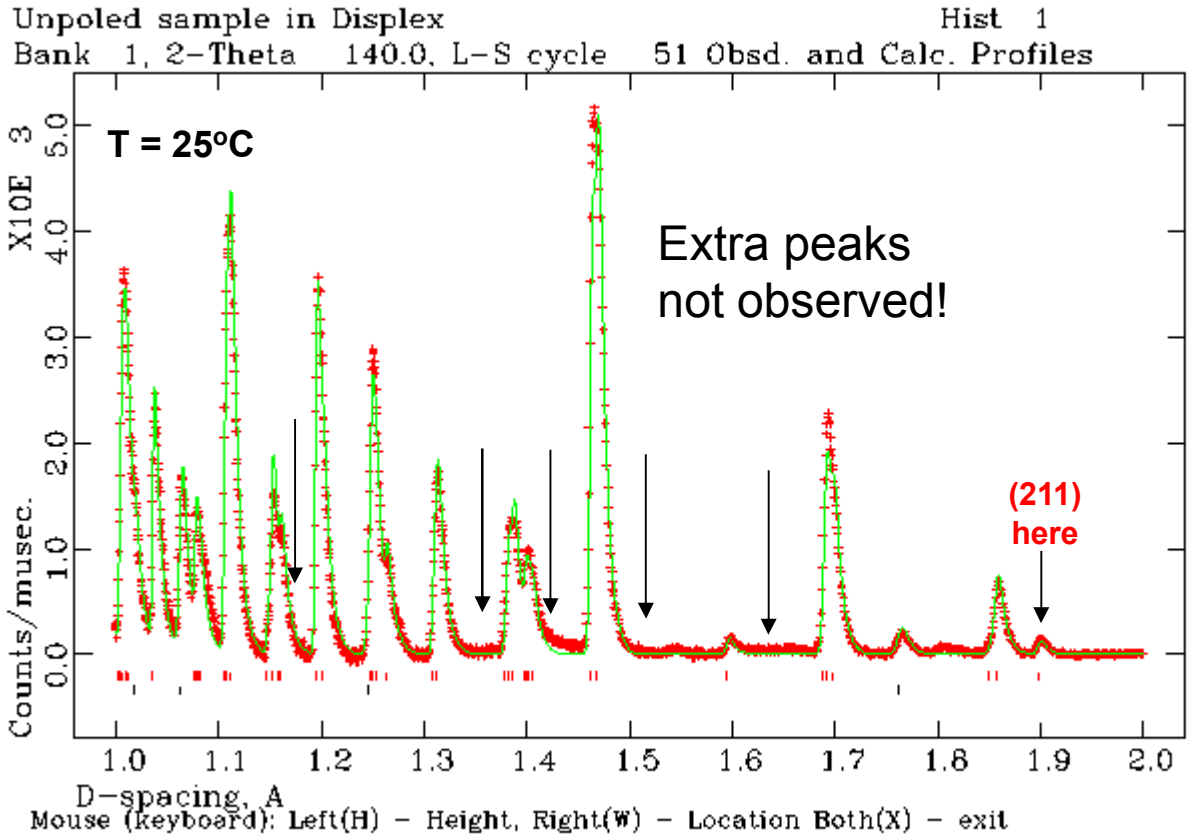


wRp = 5.46%

Rp = 3.95%

Sandia National Laboratories

A refinement of Nb-doped PZT 95/5 (T = 300 K) does not shows extra peaks.



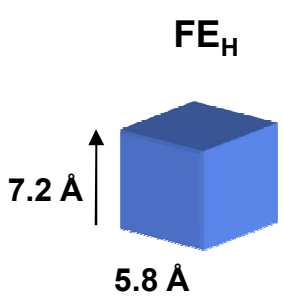
This pattern looks like a nice R3c PZT with a good fit.

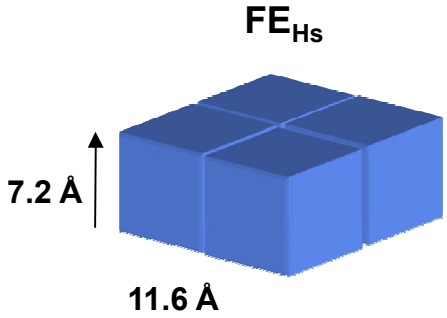
wRp = 3.77%

Rp = 2.21%

Sandia National Laboratories

By doubling the a-axis of the R3m cell, we could index the extra peaks.

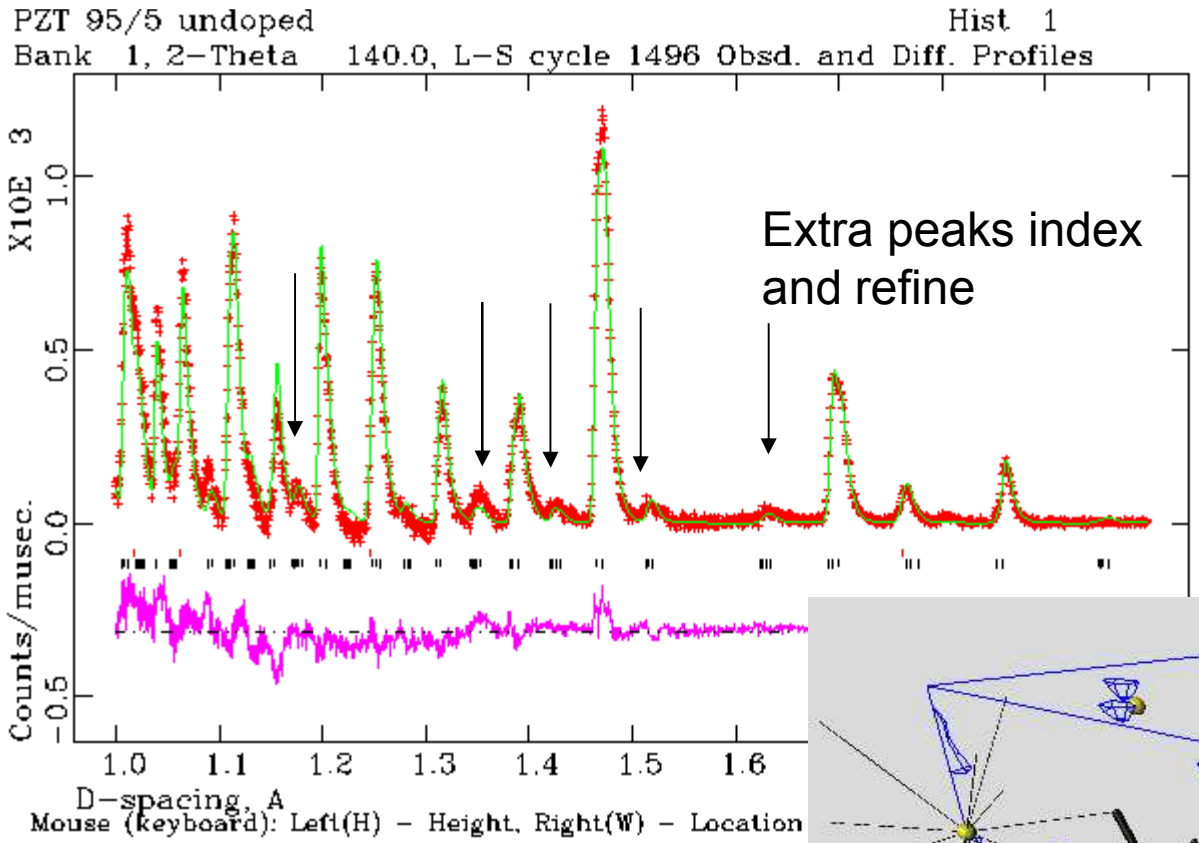




Pb1	(3a)	0	0	z	→	Pb1	(3a)	0.000 0.000 0.594
						Pb2	(9b)	0.175 0.825 0.968
Zr/Ti1	(3a)	0	0	z	→	Zr/Ti1	(3a)	0.000 0.000 0.094
						Zr/Ti2	(9b)	0.166 0.834 0.426
O1	(9b)	x	y	1/6	→	O1	(9b)	0.090 0.180 0.227
						O2	(9b)	0.916 0.832 0.896
						O3	(18c)	0.323-0.083 0.225

New cell has two *independent* sites for Pb and Zr/Ti cations and three independent O atoms.

Refinement of undoped PZT 95/5 (T = 300 K) using new superlattice cell improves refinement.



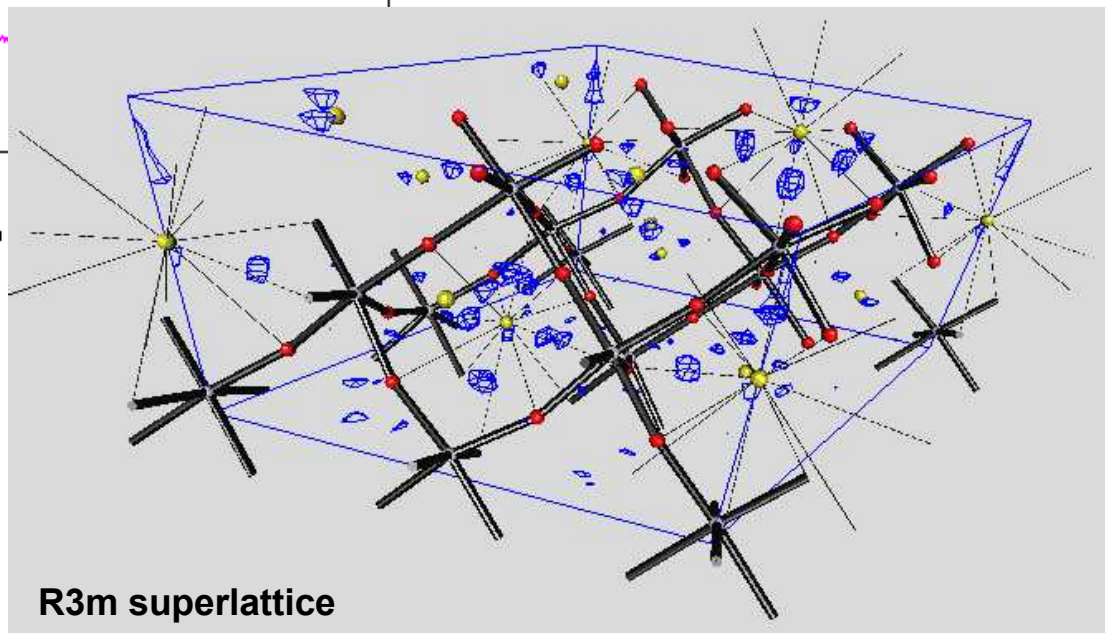
Extra peaks index and refine

FE_{Hs}

R3c → **R3m superlattice**

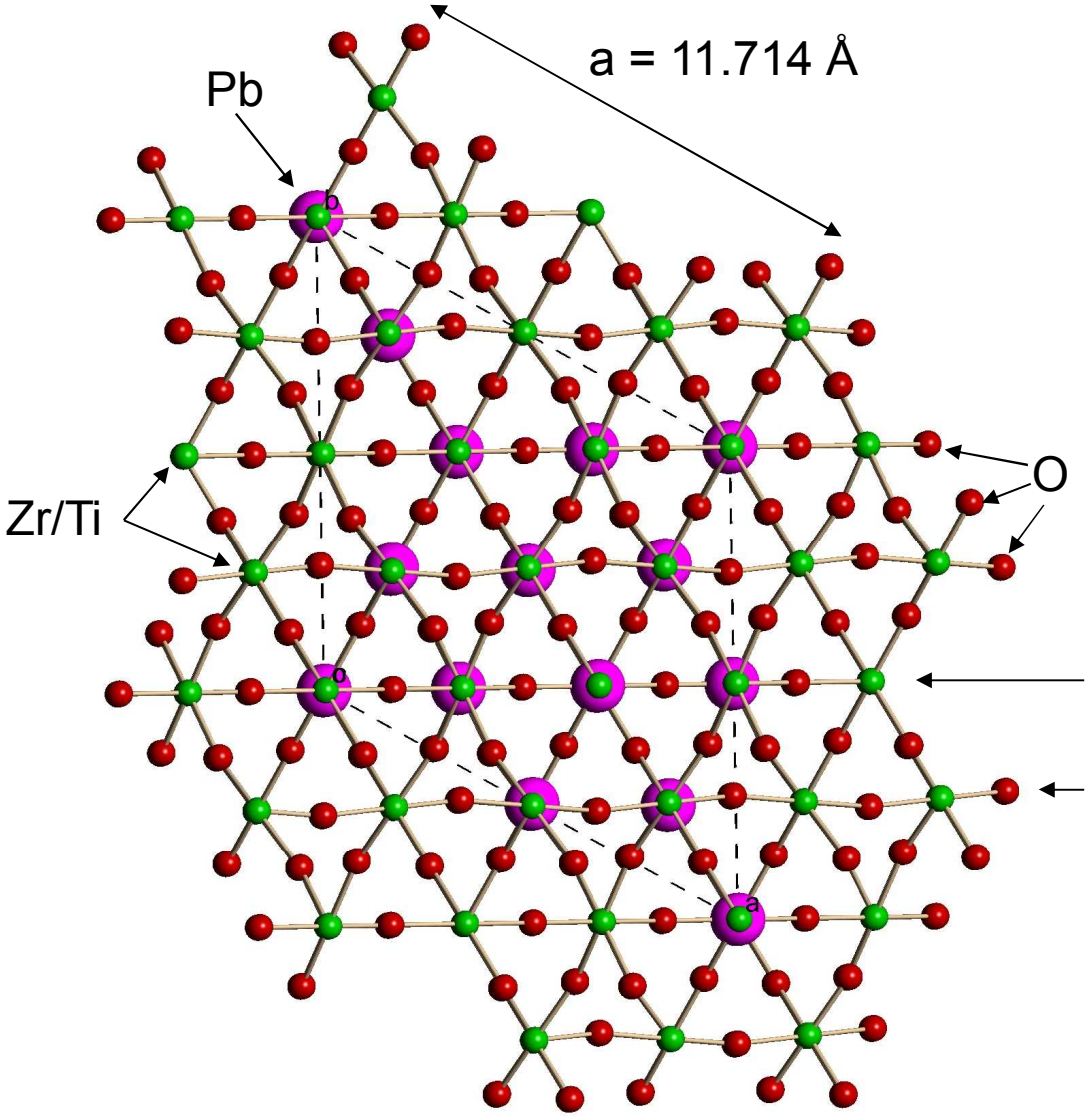
wRp = 5.46% → wRp = 4.68%

Rp = 3.95% → Rp = 3.37%

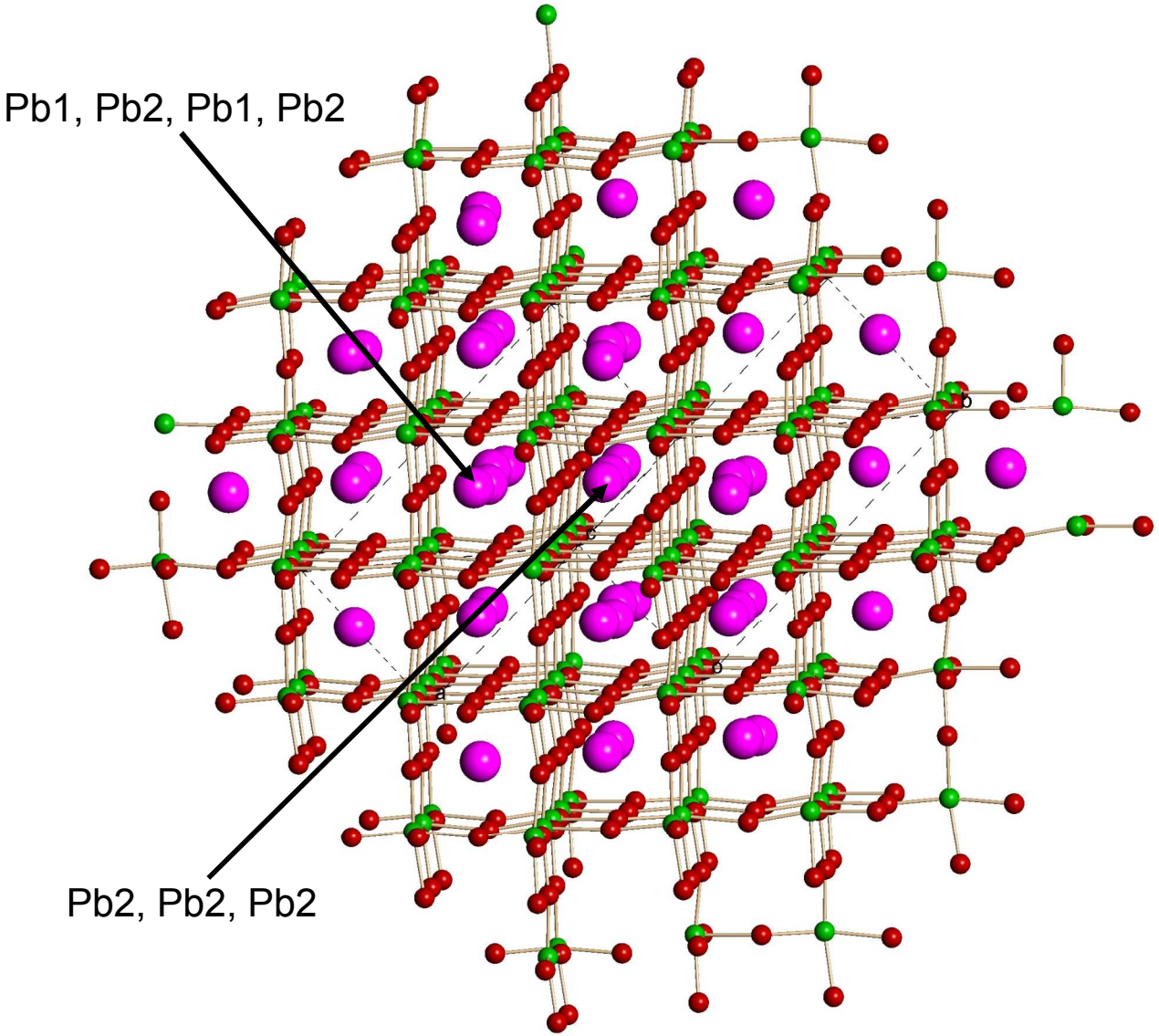


R3m superlattice

View down c-axis of new superlattice shows effect of two independent sites for the "B-site" (i.e. Zr/Ti) cations.



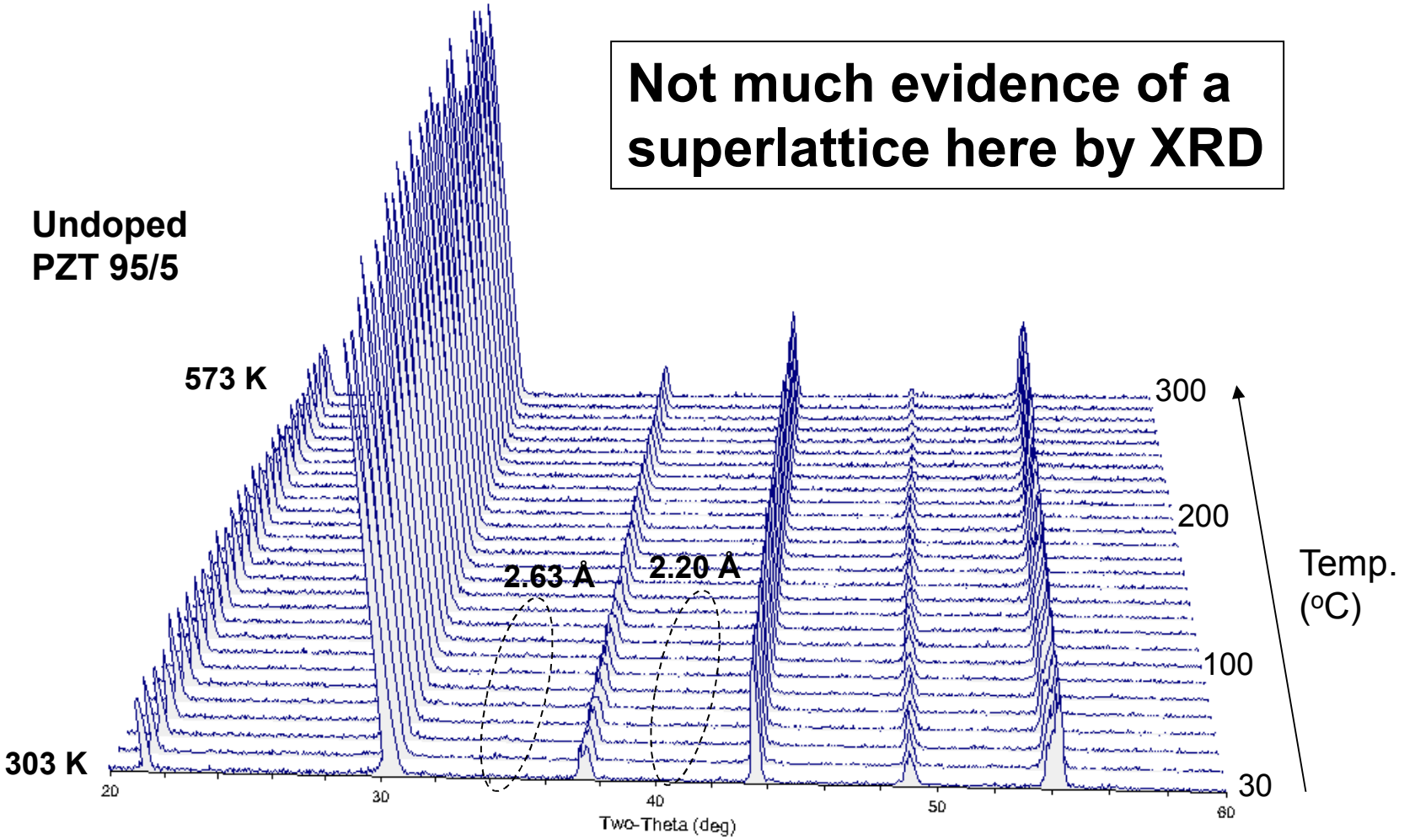
Another view shows the effect of two unique "A-site" (i.e. Pb) cations on the PZT structure.



Two unique Pb positions generate an oscillation of Pb atoms for every other simple cube.

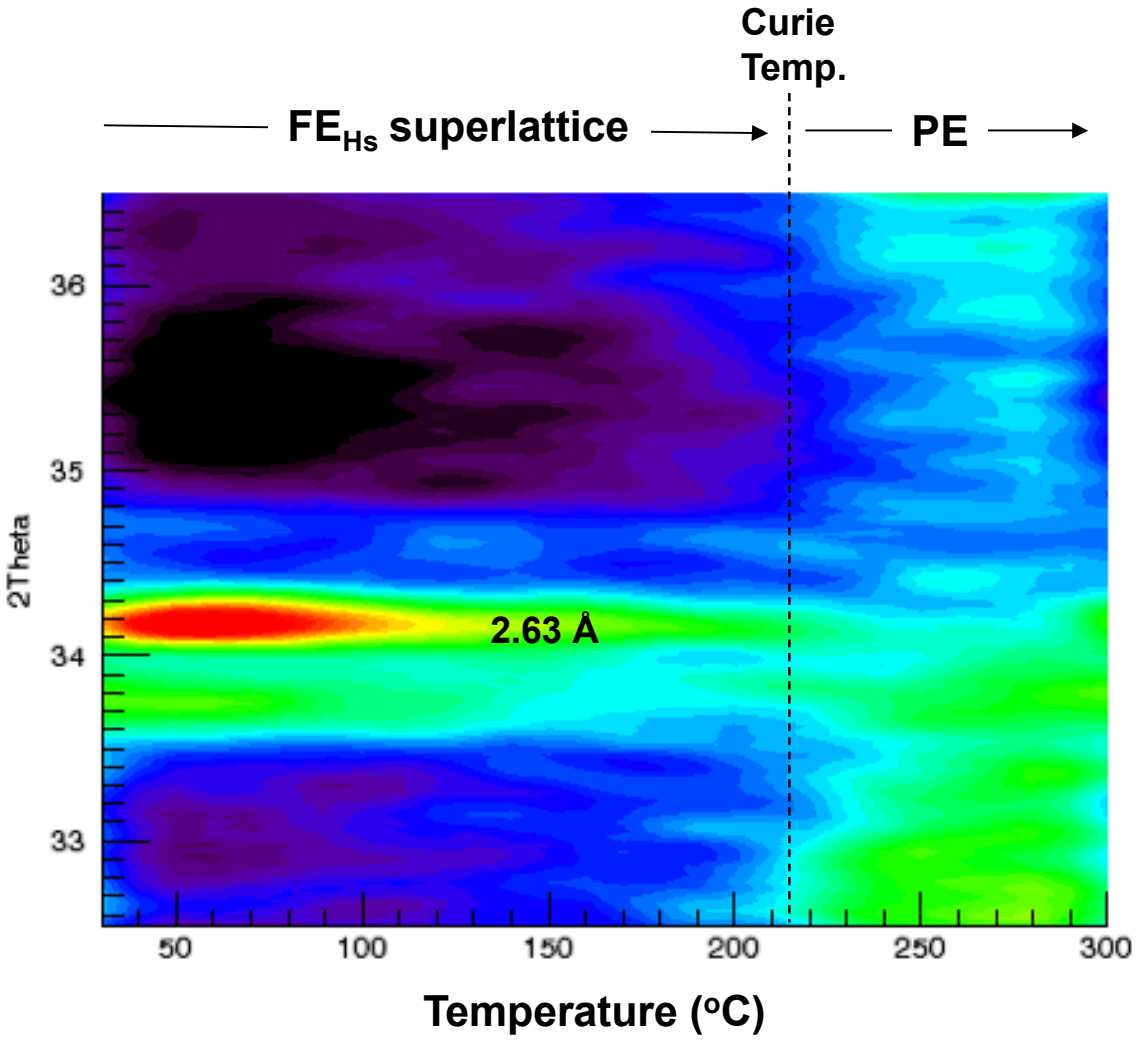
If such a superlattice exists, could I be able to pick this up using high temperature XRD?

Not much evidence of a superlattice here by XRD



Count time = 1 sec

Persistence pays off: very weak superlattice peak is observed above background for Undoped PZT 95/5 sample.



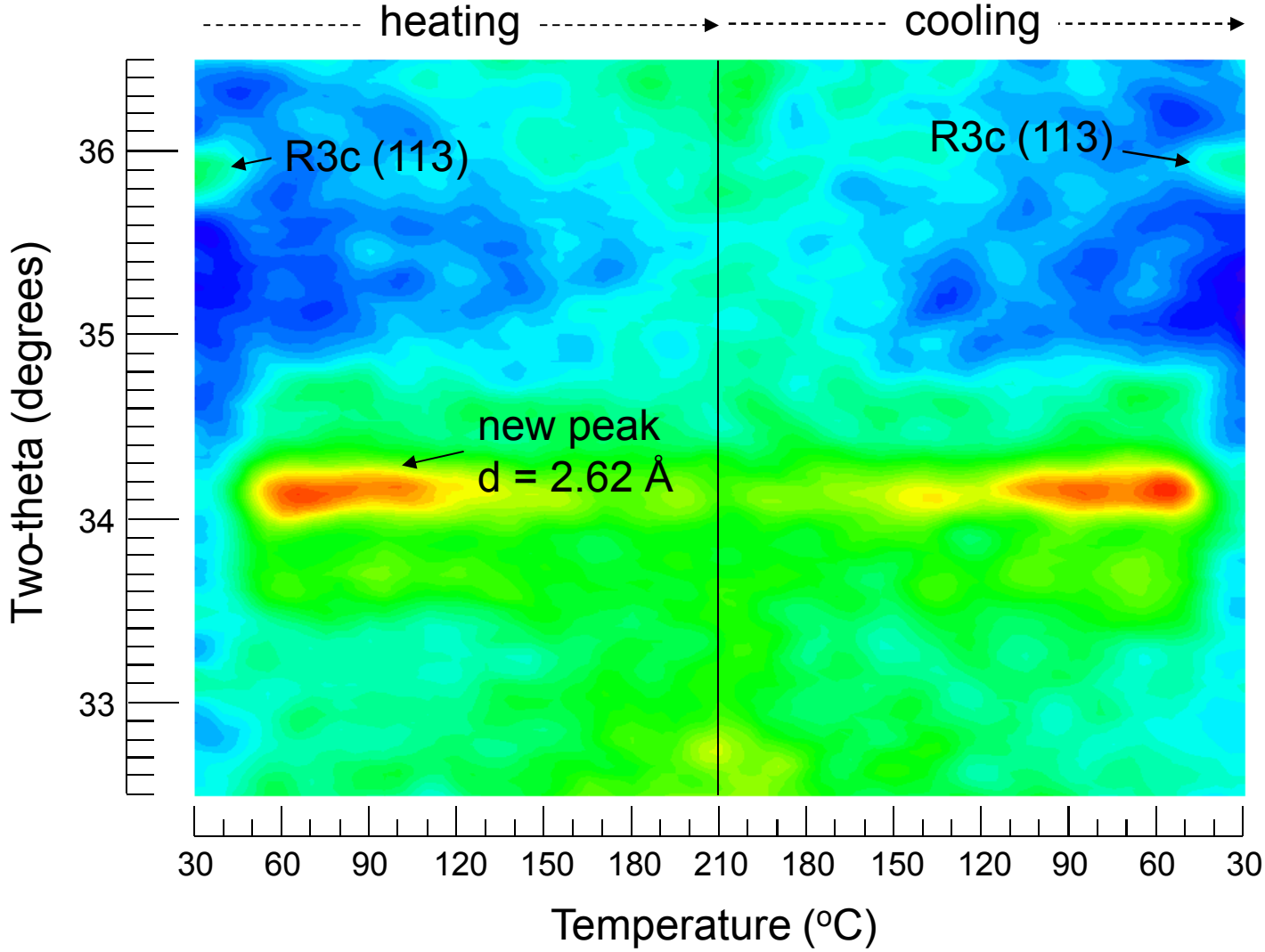
XRD data for Undoped sample PZT 95/5

0.04 °2θ step-size
60 s count-time
32.5 - 36.5 °2θ range

30 hrs total time

Sandia National Laboratories

Nb-doped PZT 95/5 also shows very weak peak. Cycling reveals R3c to R3m superlattice phase transition at ~50 °C.



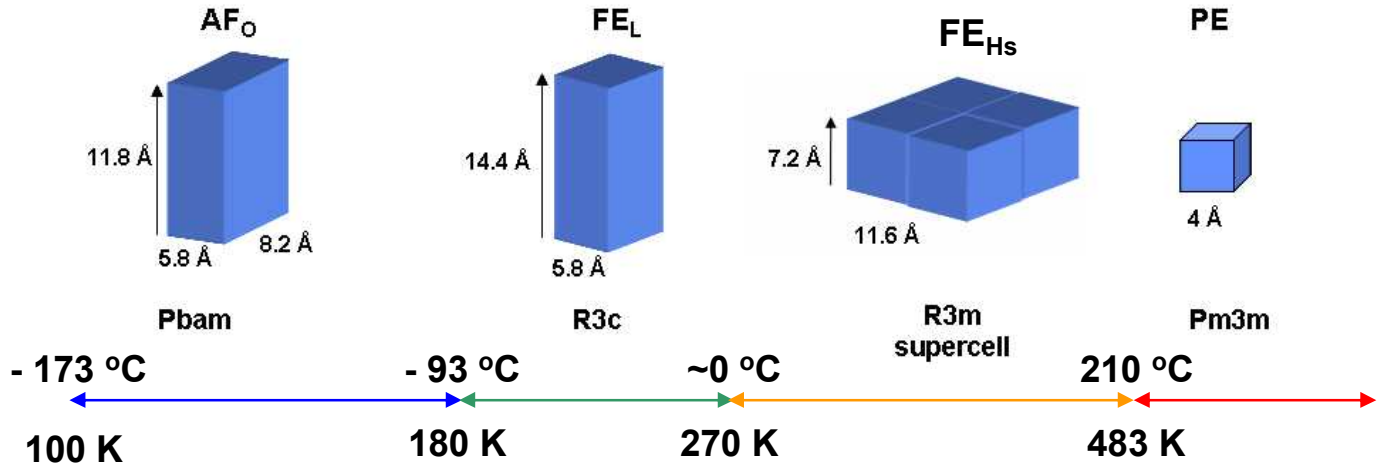
XRD data for Nb-doped sample PNZT 95/5

0.04 °2θ step-size
60 s count-time
32.5 - 36.5 2θ range

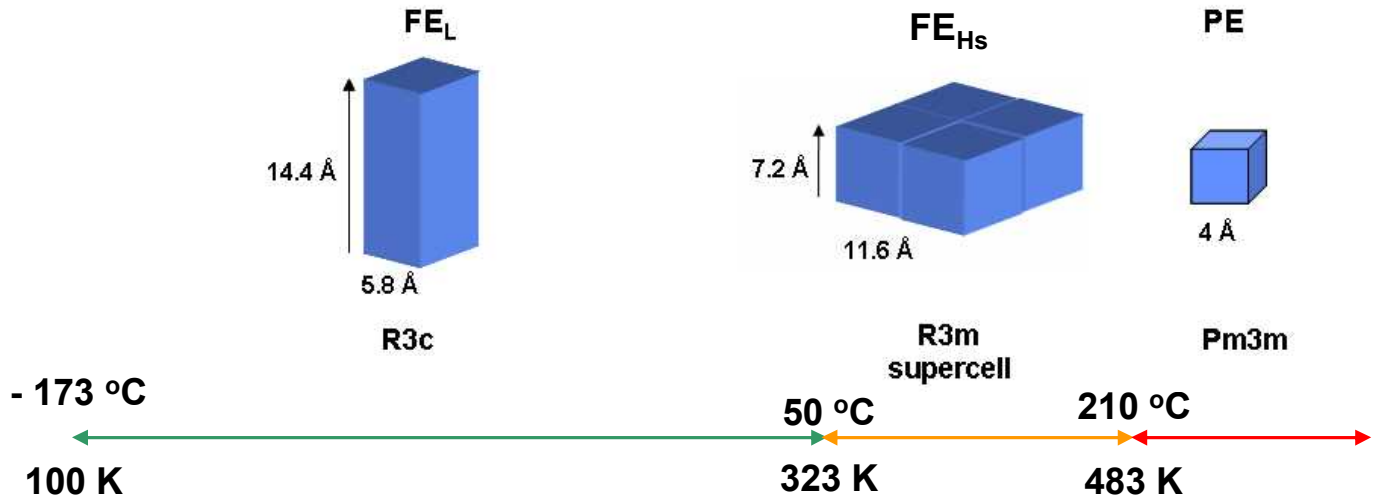
60 hrs total time

Sandia National Laboratories

Combination of in-situ XRD and neutron diffraction data shows the following picture.



Undoped PZT 95/5



Nb-doped PZT 95/5

Sandia National Laboratories

Summary

- In-situ neutron diffraction via the HIPPO spectrometer worked well for the study of PZT 95/5 materials.
- There were no major structural changes for Nb-doped PZT 95/5 between 100 K and 300 K.
- We observed new peaks in both Nb-doped and undoped PZT 95/5 which could be indexed to a new superlattice R3m cell (i.e. FE_{Hs}).
- Superlattice doubles a-axis of FE_H structure, which results in two unique sites for A-site and B-site cations.
- With sufficient statistics, it was possible to observe FE_{Hs} superlattice peaks using High-temperature XRD.