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SIZE AND SYNTHESIS EFFECTS ON THE CRYSTALLINE STRUCTURE OF BARIUM TITANATE NANOPARTICLES

ACCGE-20

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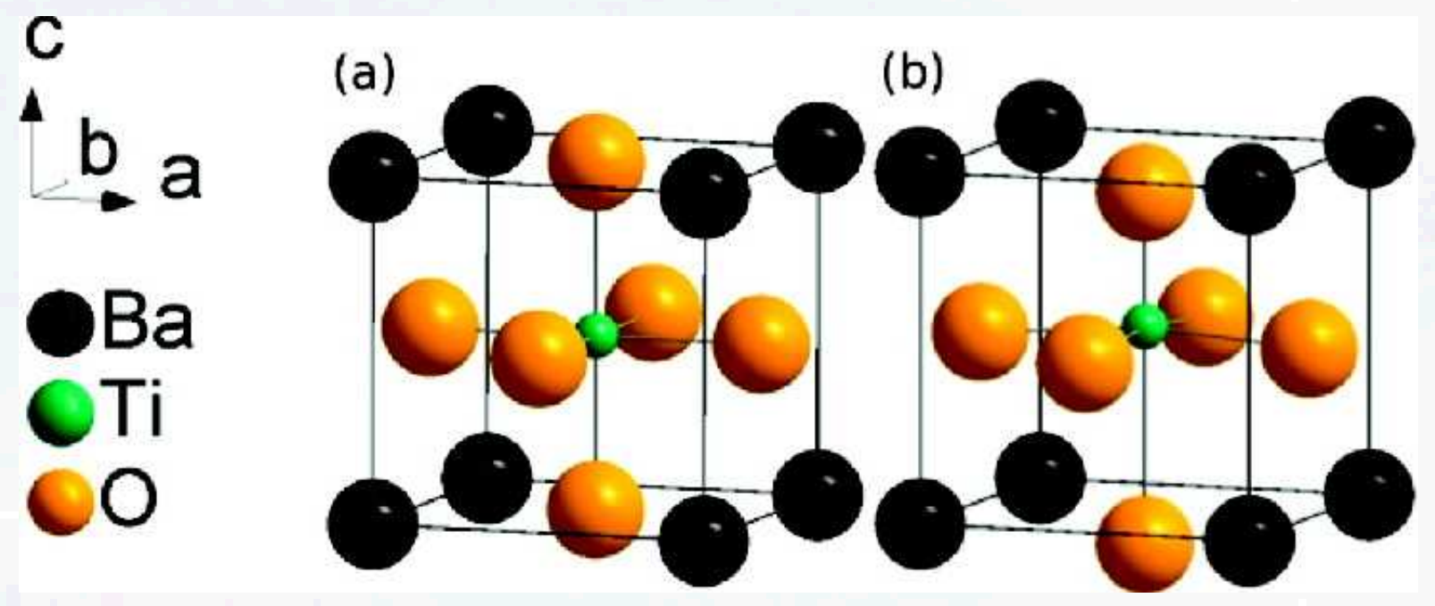
Introduction

Ferroelectric nanoparticles, in particular barium titanate (BTO), exhibit bewildering behavior at the nanoscale. In most sintered, fully dense devices, their permittivity drops off with decreasing grain size from a maximum at ~1 μm and larger grain sizes. However, when BTO particles remain unsintered and are studied in solution or some other matrix material, their permittivity has been shown (although these results remain controversial) to increase dramatically as a critical diameter is approached, after which the particles' permittivity falls precipitously with further decreases in size. Even below this critical size where measured permittivity values of BTO nanoparticles are extremely low and approach zero, some BTO samples have been shown to have tetragonal crystallographic distortions at the local level. However, these tetragonal distortions are not maintained coherently across the entire width of the particle, resulting in a macroscopic crystal structure that resembles a cubic lattice. To date, little is known about how synthesis methods, passivating ligands, and other physical properties of BTO nanoparticles affect their behavior at the nanoscale.

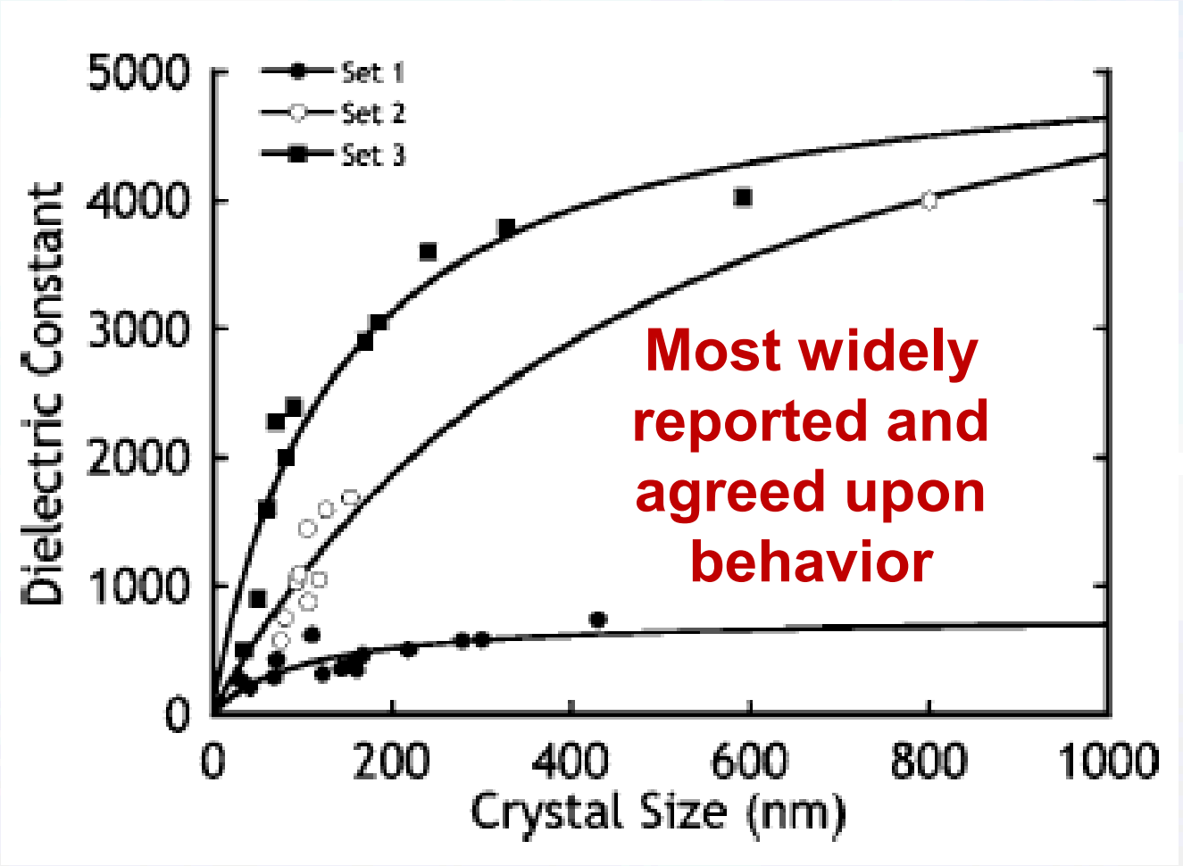


(a) Cubic Pm-3m structure
(b) Tetragonal P4mm structure

Smith et. al., J. Am. Chem. Soc. 130 (2008) 6955-6963

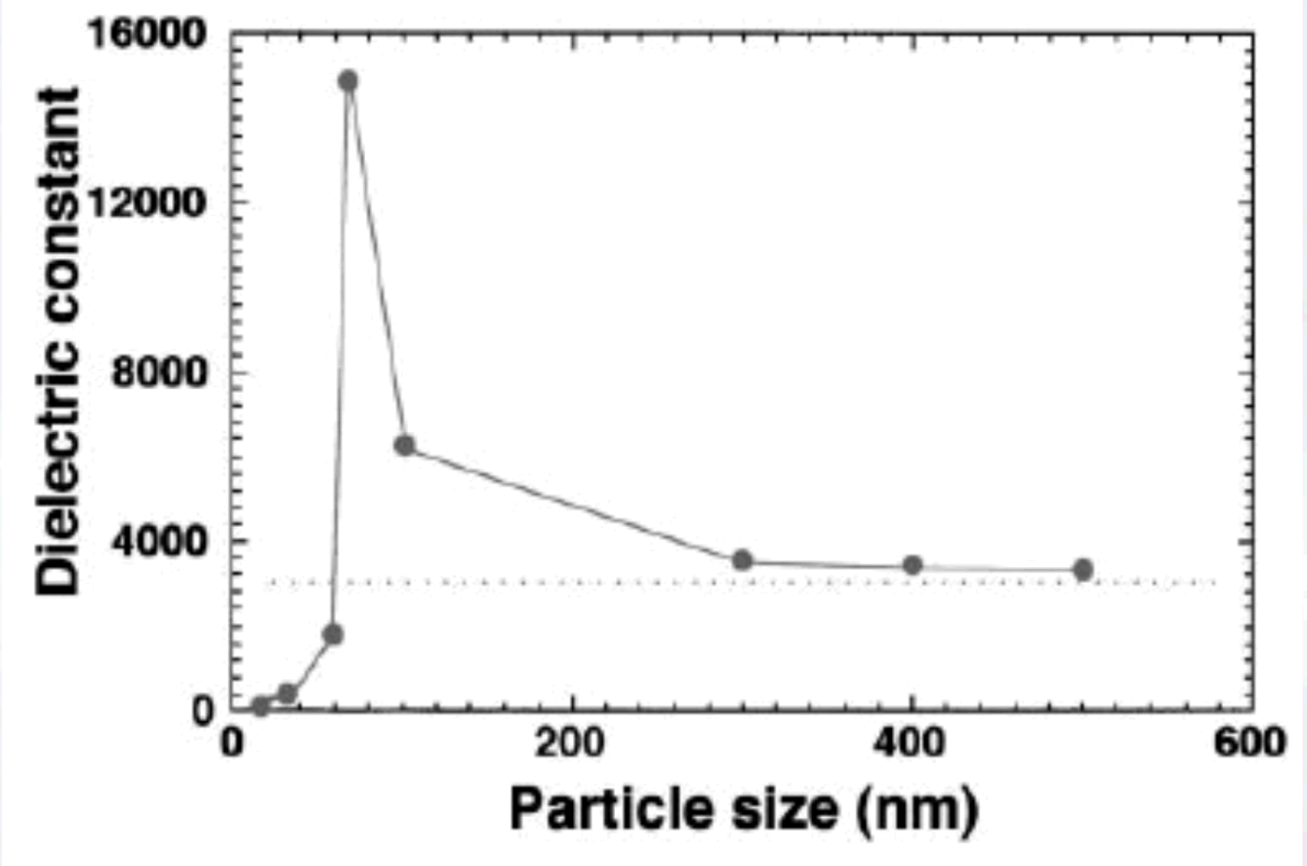
Bulk BTO exhibits a tetragonal phase at room temperature. Spontaneous polarization of the unit cell is due to both a stretching of one axis and a displacement of the Ti^{4+} ion . A tetragonal (T) to cubic (C) phase transition occurs at 125°C. For nanoparticles, T and C phases may coexist.

Behavior of Nanosized $BaTiO_3$



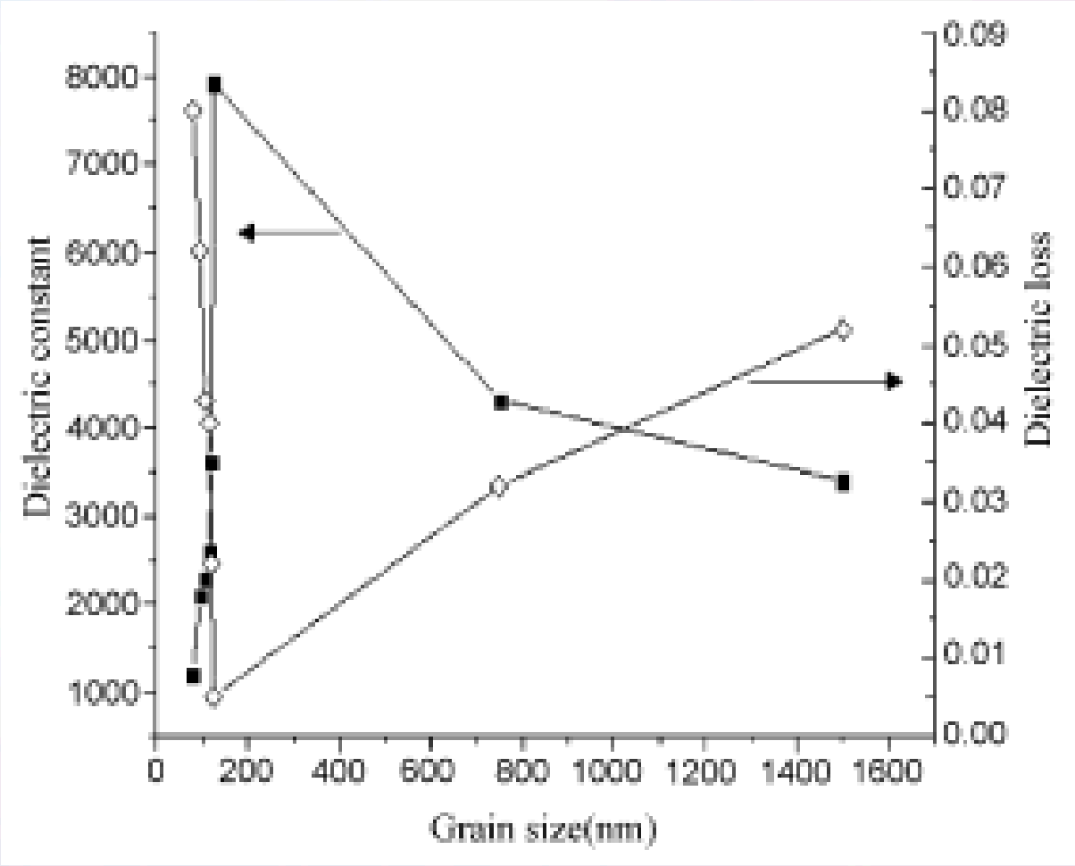
Sintered $BaTiO_3$

Aygün et. al., J. Appl. Phys. Vol. 109 (2011) 034108



$BaTiO_3$ particles in solution

Wada et. al., Jpn. J. Appl. Phys. Vol. 42 (2003) 6188–6195

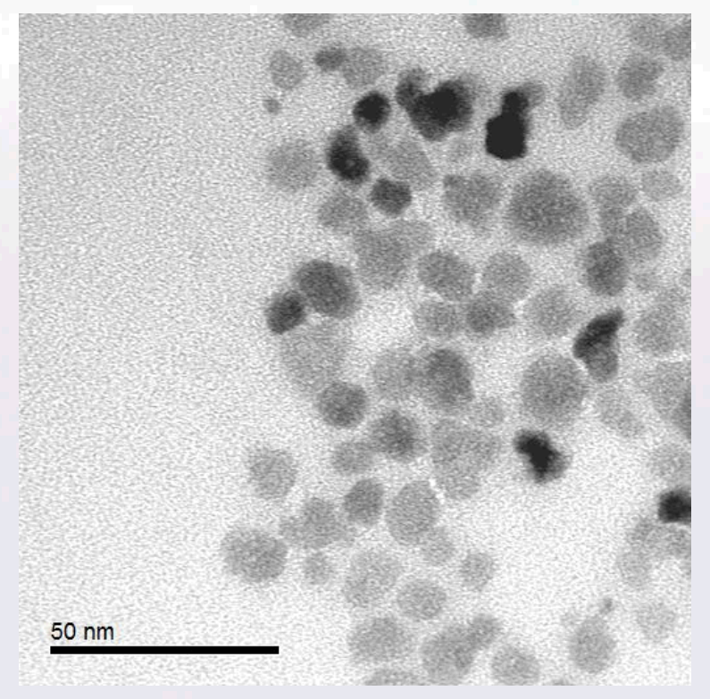


Sintered $BaTiO_3$

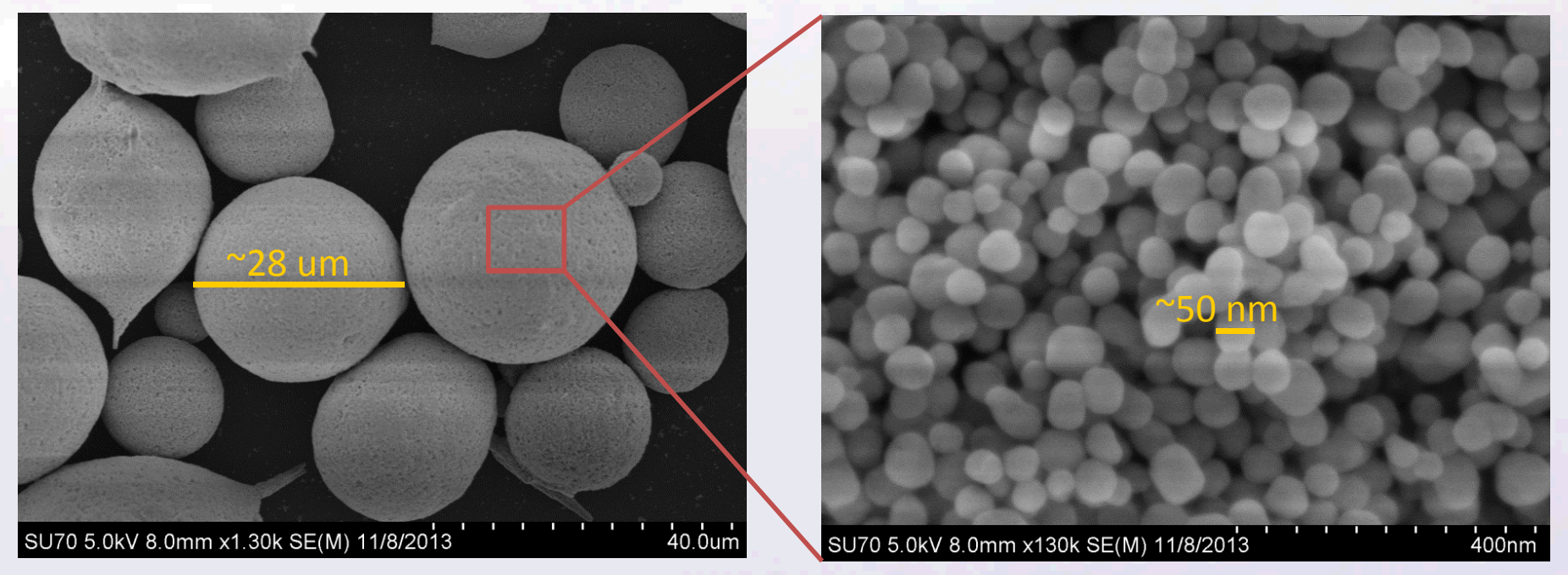
Ying and Hsieh, Materials Science and Engineering B 138 (2007) 241–245

The Particles

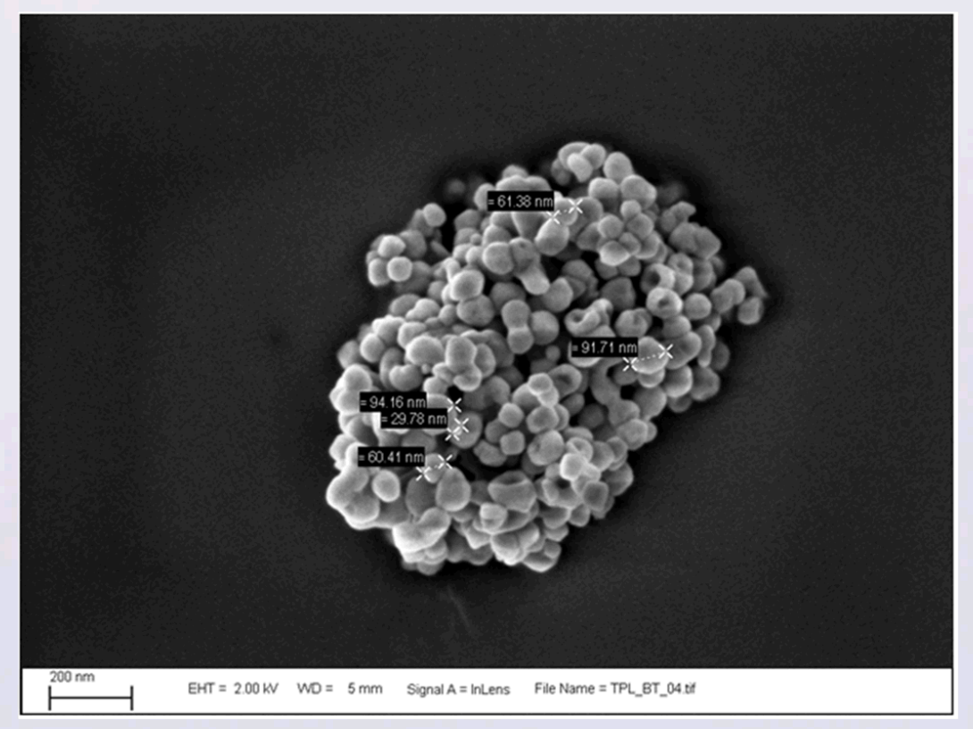
Source	Name	Primary Particle Diameter (nm)	Synthesis Method
Sandia	SNL	10	80°C solution
TPL	HPB-1000	50	hydrothermal
Sakai	KZM-50	50	hydrothermal
Sakai	BT-01	100	hydrothermal
Sakai	BT-02	200	hydrothermal
Sakai	BT-03	300	hydrothermal
Sakai	BT-04	400	hydrothermal
Sakai	BT-05	500	hydrothermal



Sandia solution synthesized $BaTiO_3$

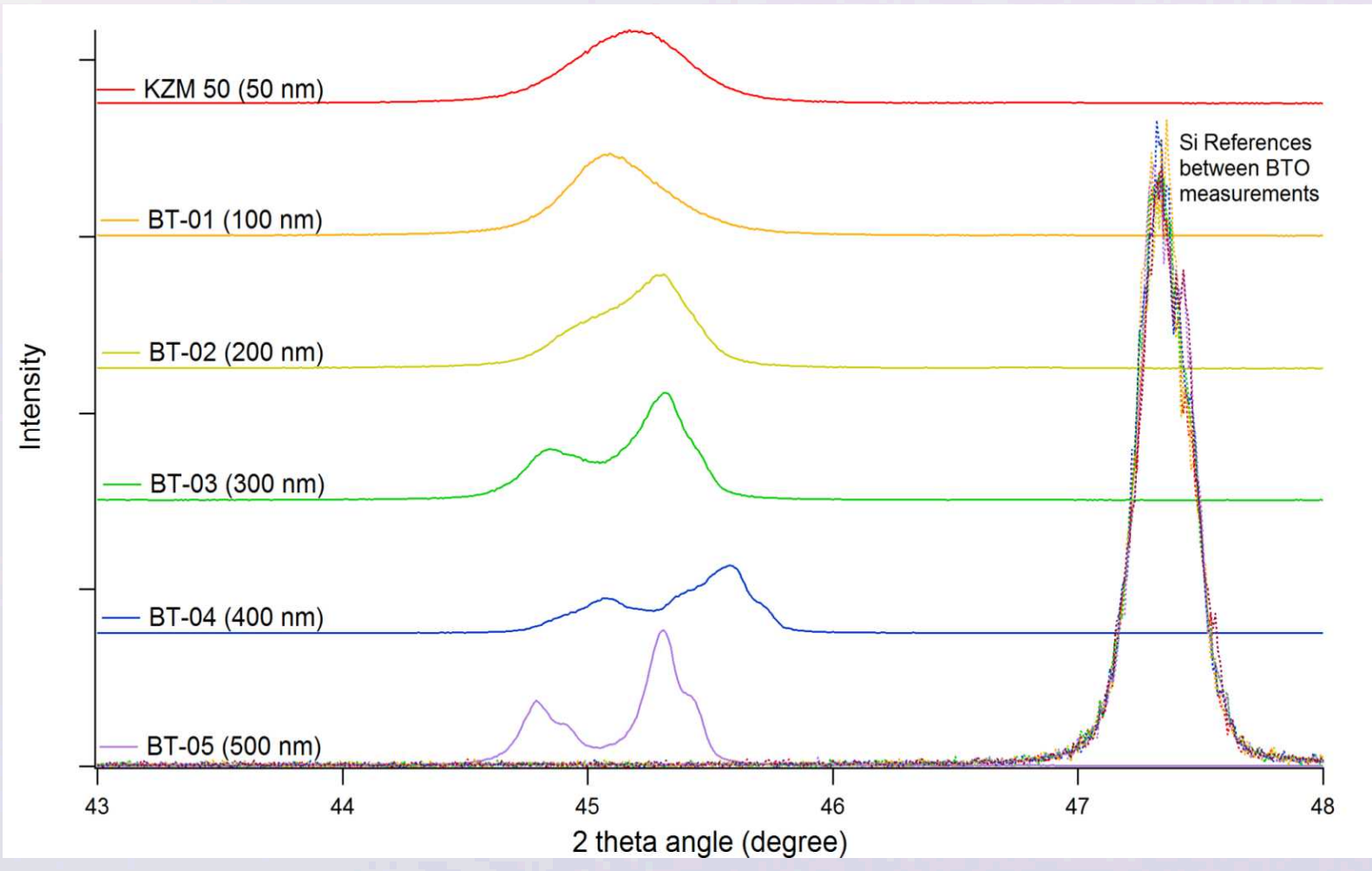


Sakai KZM-50



TPL NanOxide HPB-1000

Powder X-Ray Diffraction (XRD)



XRD measures a cubic structure for 50 and 100 nm particles. For particles larger than 200 nm, the [200] peak is split, indicating an asymmetry along one axis (tetragonality)

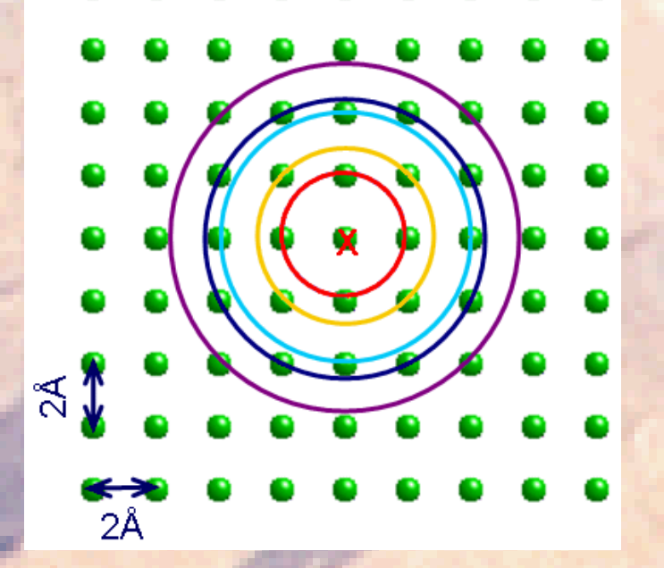
High Energy X-Ray Scattering at NSLS (Brookhaven National Lab), analyzed via the atomic Pair Distribution Function (PDF)

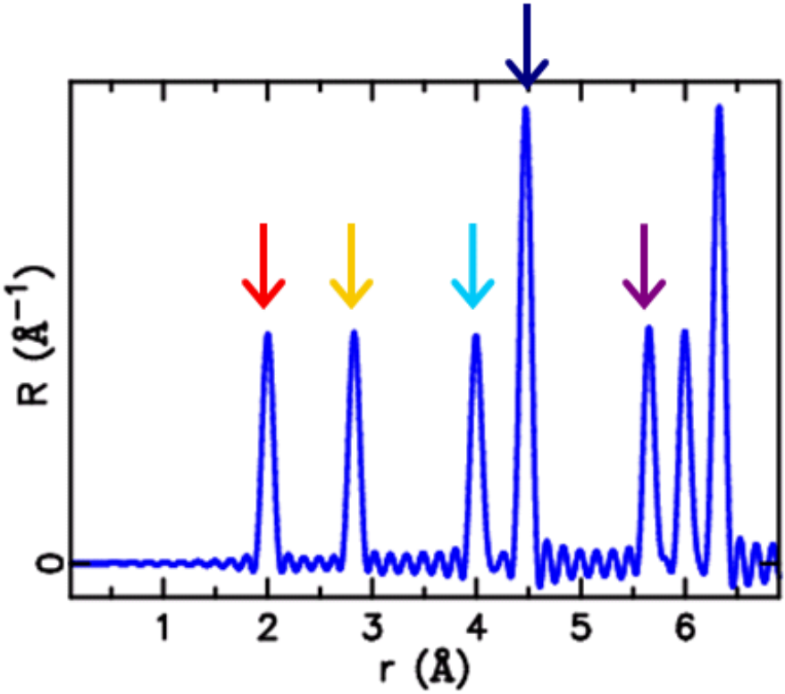
Introduction to PDF

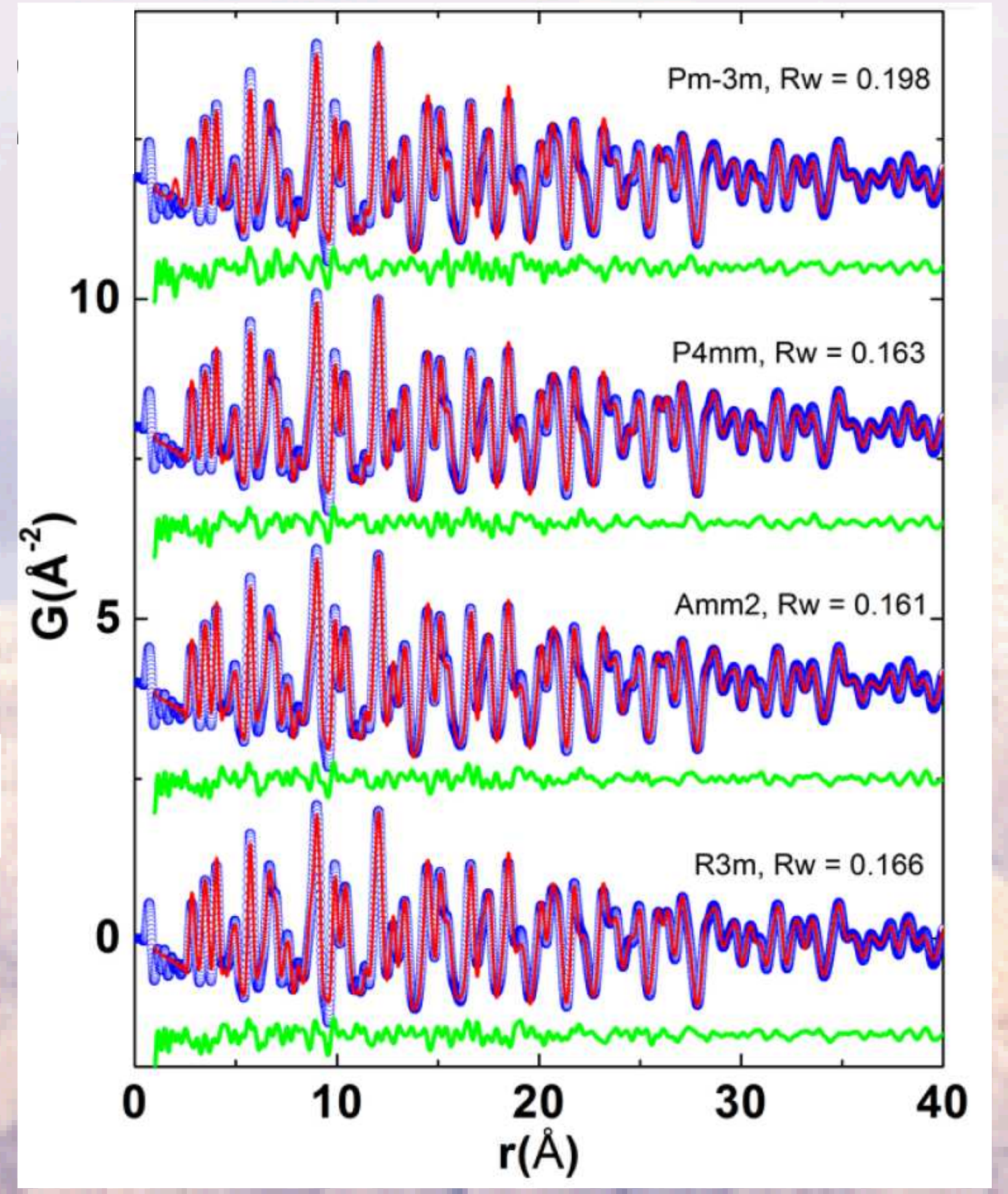
The atomic Pair Distribution Function (PDF) is the probability of one atom finding a neighboring atom at a distance "r". The PDF makes no assumption about periodicity, evaluating all intensities from both Bragg and diffuse scattering. It is obtained by a Fourier transformation of powder diffraction data and its relationship to a material's structure is:

$$G(r) = 4\pi r\left[\rho(r) - \rho_0\right] = \frac{1}{Nr}\sum_{m \neq n}\frac{b_m b_n}{\langle b \rangle^2}\,\delta\left(r - r_{mn}\right) - 4\pi r \rho_0$$

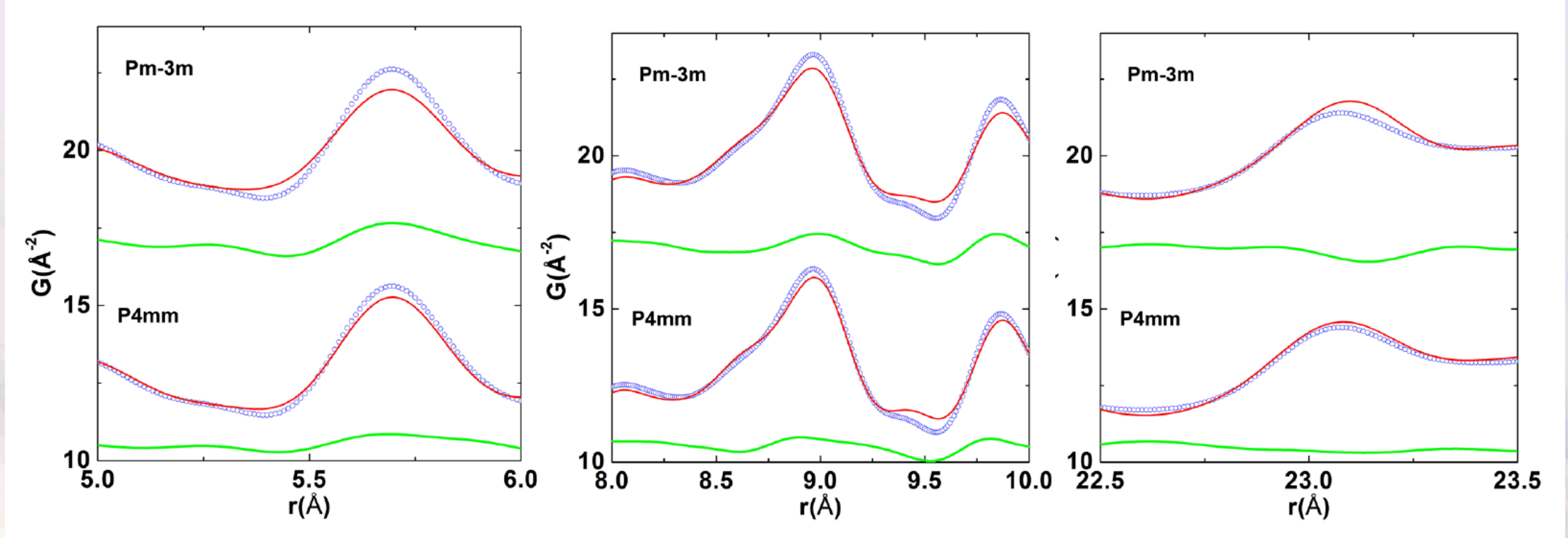
Farrow and Billinge, Acta Cryst. A Vol. 65 (2009) 232-239





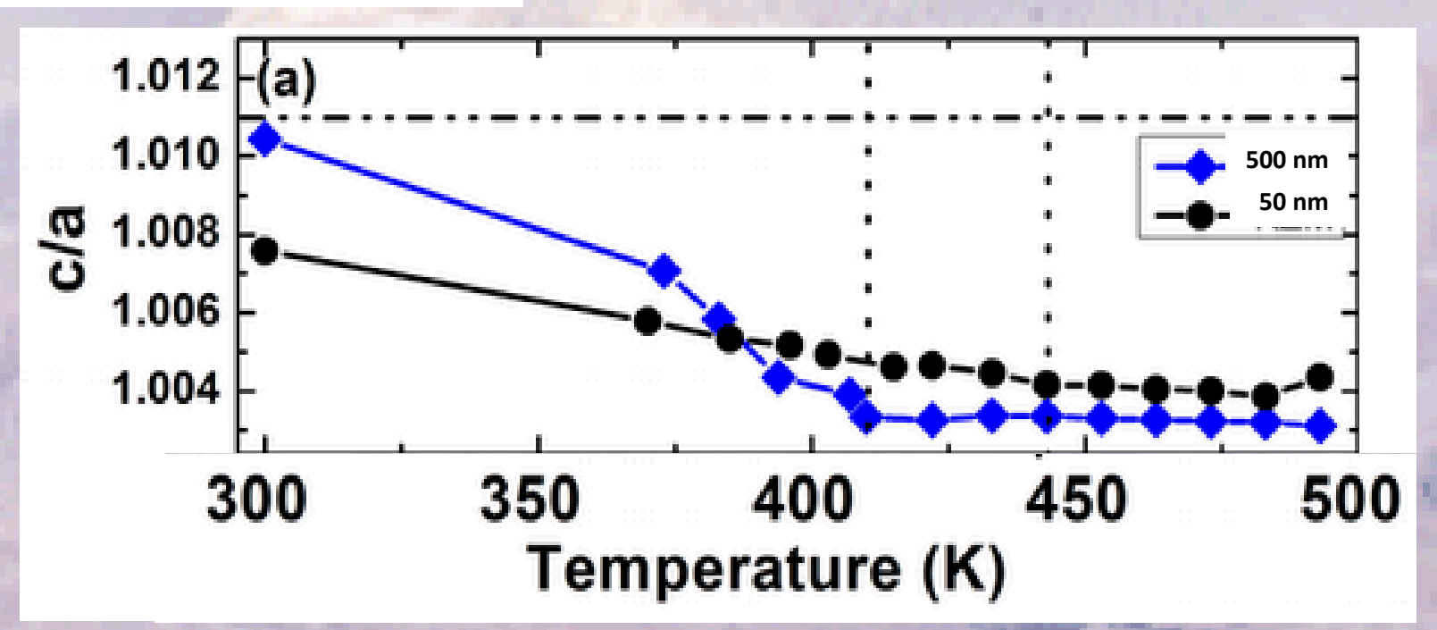


PDF model fits to Sandia $BaTiO_3$ nanoparticles measured at 300 K with four different candidate space groups. Blue circles are the measured data, red curves are the calculated PDFs of the best-fit structural models, and the green curves offset below are difference curves.



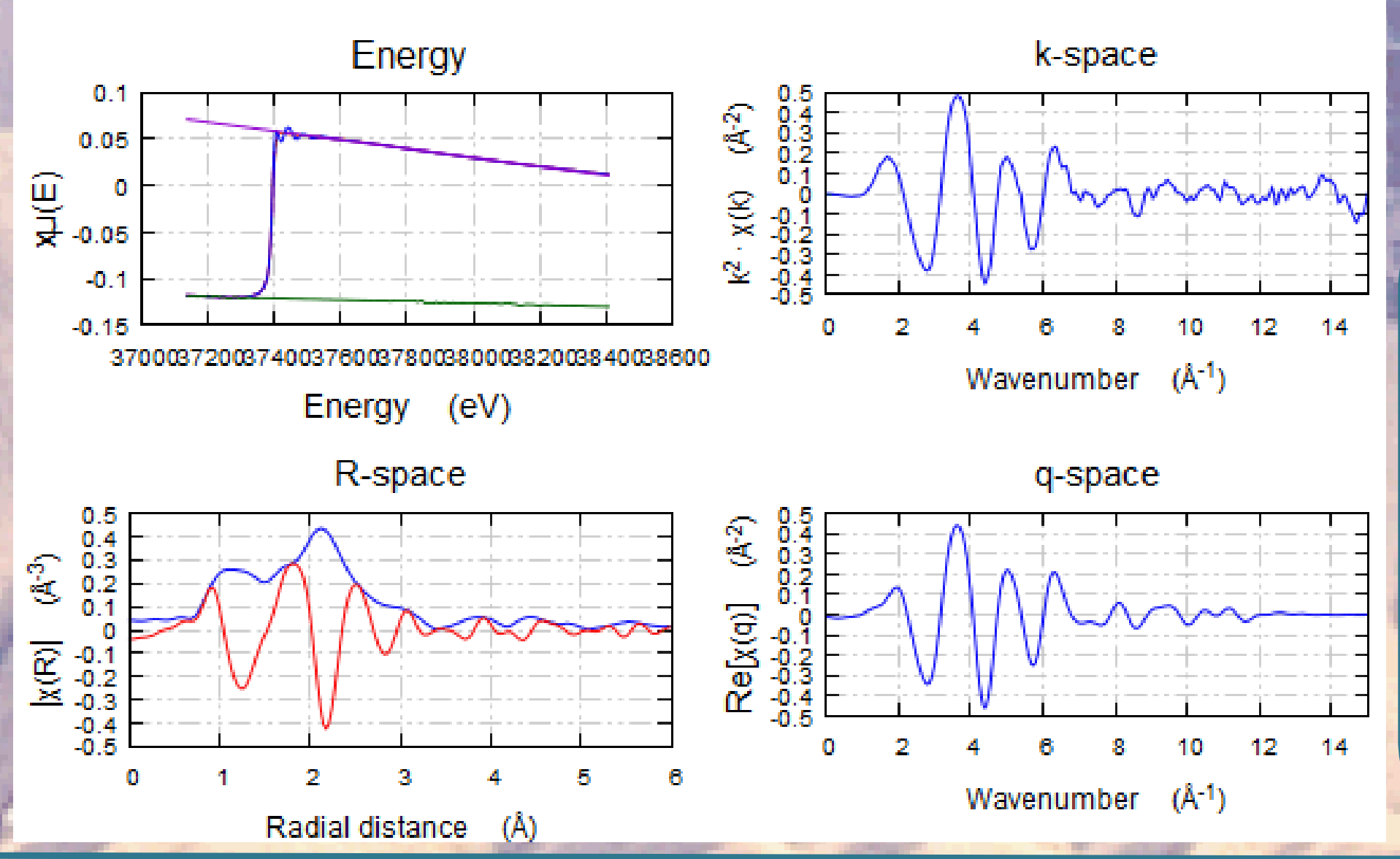
Expanded PDF fits (red) to experimental PDF data (blue) of SNL $BaTiO_3$ nanoparticles at 300 K using cubic (top) and tetragonal (bottom) phase groups. The tetragonal fit is visibly superior.

Measurements from the National Synchrotron Light Source (BNL) demonstrate reduced tetragonality at room temperature for 50 nm particles and confirm the diffuse and incomplete T → C transition suggested in Raman.

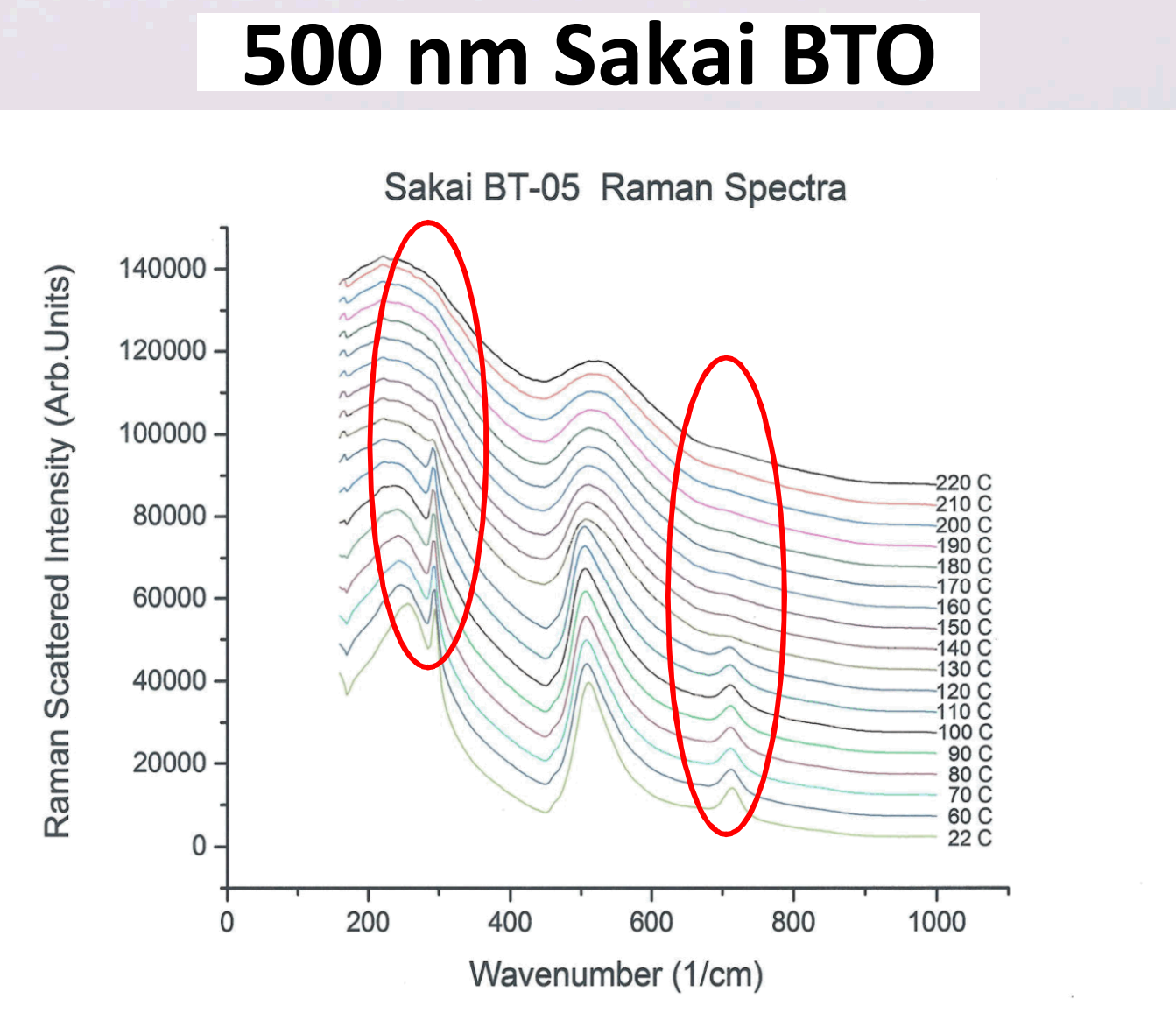


XAFS at APS (Argonne National Lab):

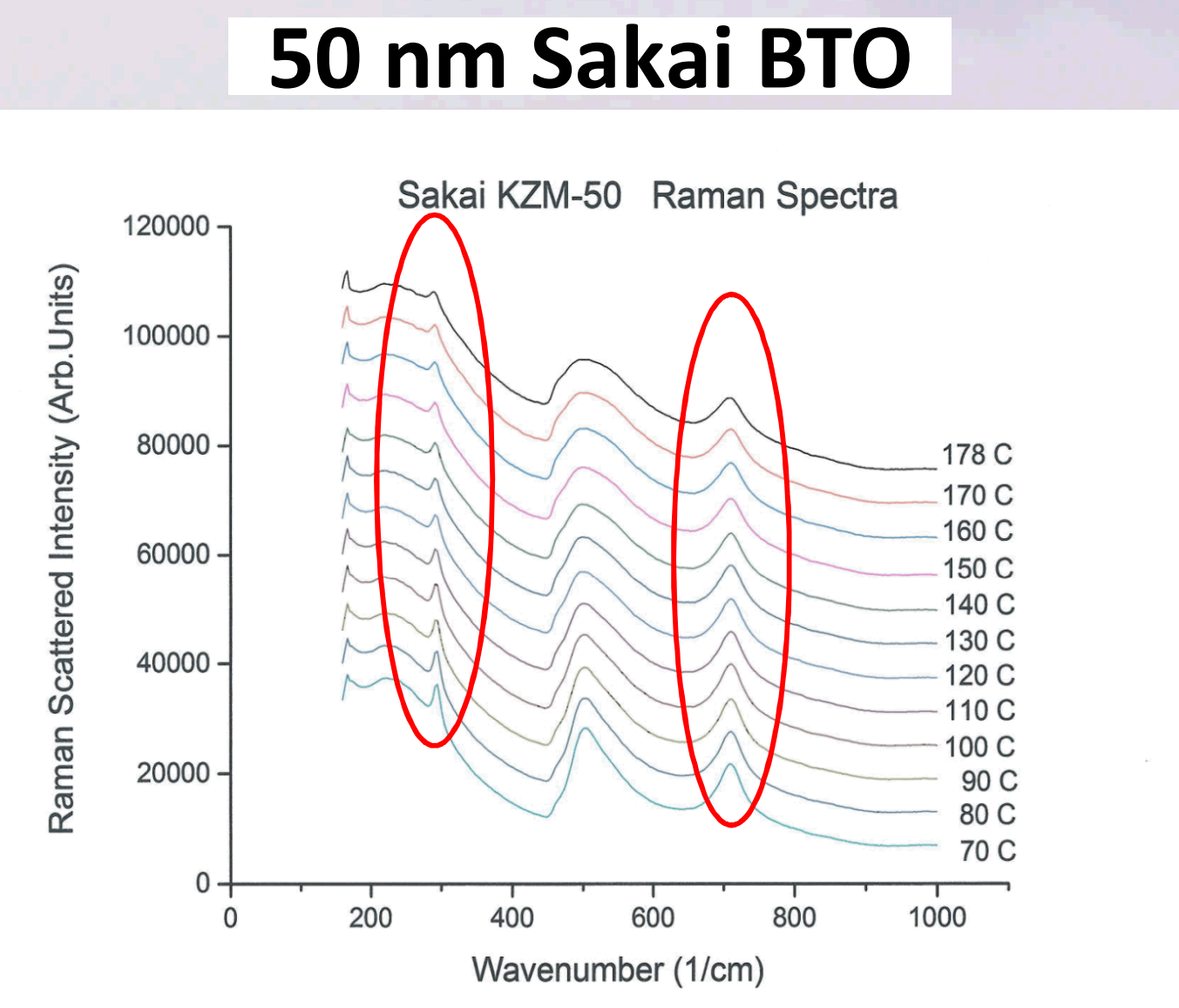
Collected but still being fit!



Raman Spectroscopy



For 500 nm BTO, as in bulk, the $300 cm^{-1}$ and $710 cm^{-1}$ peaks disappear sharply at the T → C transition temperature (125°C).



For 50 nm BTO, these peaks remain, suggesting persisting tetragonality at elevated temperatures.

Conclusions:

- Particles > 200 nm behave metrically tetragonal
- Particles < 200 nm have a distorted tetragonal (or possibly other) structure
  - Diffuse phase transition
  - Possible disordered coexistence of phases

Future Work:

- Analyze XAFS data for more insight into local BTO structure
- Study the effect of surface functionality (ligands) on the crystal structure of SNL BTO nanoparticles

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