STUDYING FERROELECTRICITY AT THE NANOSCALE USING HIGH ENERGY X-RAYS

63rd Annual Denver X-ray Conference

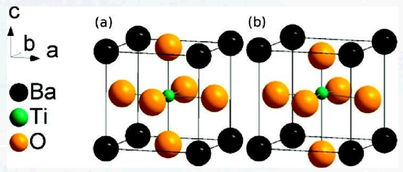
Todd C. Monson[1*], Sun Hwi Bang[2], Nate Bean[2], Jean-Claude de Sugny[2], Robert Gambee[2], Eric Puma[3], Richard Haskell[2], Adrian Hightower[2], Chenyang Shi[4], Simon Billinge[4], Qing Ma[5]

[1]Sandia National Laboratories, Albuquerque, NM, USA *Email: tmonson@sandia.gov; [2]Harvey Mudd College, Claremont, CA, USA; [3]Pomona College, Claremont, CA, USA; [4]Columbia University, New York, NY, USA; [5]DND-CAT, Advanced Photon Source, USA

SAND2014-16388D

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 distorted 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.

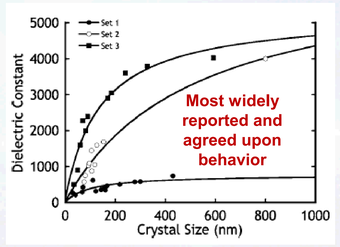


(a) Cubic Pm-3m structure
(b) Tetragonal P4mm structure

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

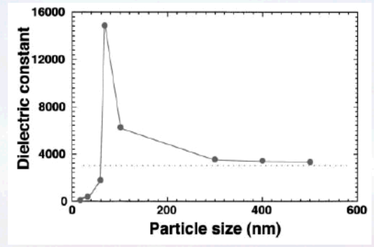
Bulk BTO exhibits a tetragonal phase at room temperature. Spontaneous polarization of the unit cell is due to both a stretching of one axis and a displacement of the Ti^{4+} ion . A tetragonal (T) to cubic (C) phase transition occurs at 125°C. For nanoparticles, T and C phases may coexist.

Behavior of Nanosized $BaTiO_3$



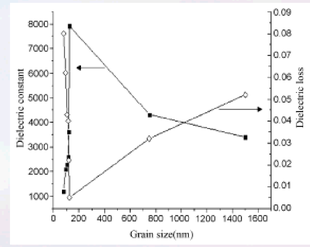
Sintered $BaTiO_3$

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

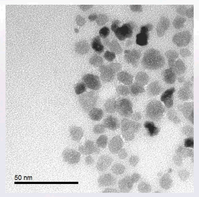


Sintered $BaTiO_3$

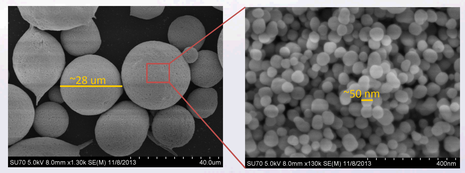
Ying and Hsieh, Materials Science and Engineering B 138 (2007) 241–245

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

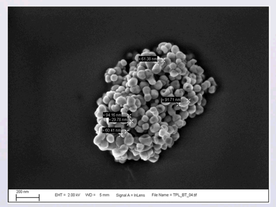
The Particles



Sandia solution synthesized $BaTiO_3$

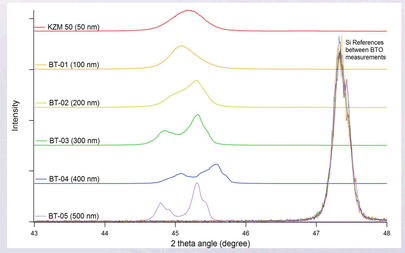


Sakai KZM-50



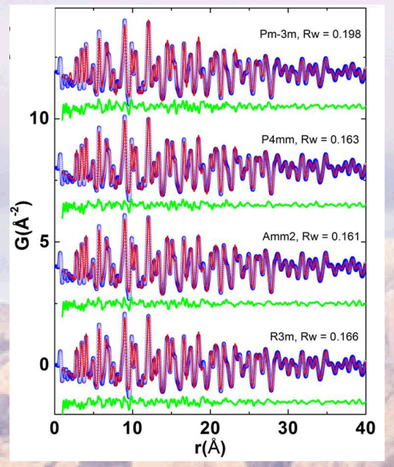
TPL NanOxide HPB-1000

Powder X-Ray Diffraction (XRD)

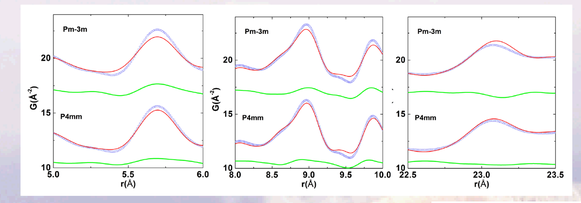


XRD measures a cubic structure for 50 and 100 nm particles. For particles larger than 200 nm, the [200] peak is split, indicating an asymmetry along one axis (tetragonality)

High Energy X-Ray Scattering at NSLS (Brookhaven National Lab)

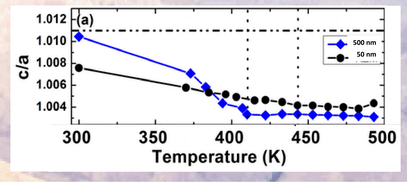


PDF model fits to Sandia $BaTiO_3$ nanoparticles measured at 300 K with four different candidate space groups. Blue circles are the measured data, red curves are the calculated PDFs of the best-fit structural models, and the green curves offset below are difference curves.



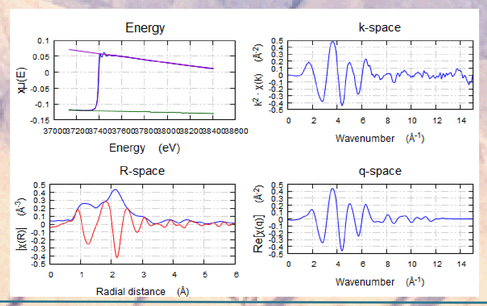
Expanded PDF fits (red) to experimental PDF data (blue) of SNL $BaTiO_3$ nanoparticles at 300 K using cubic (top) and tetragonal (bottom) phase groups. The tetragonal fit is visibly superior.

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.



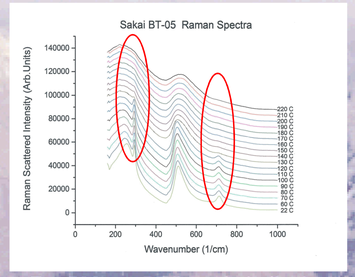
XAFS at APS (Argonne National Lab):

Collected but still being fit!



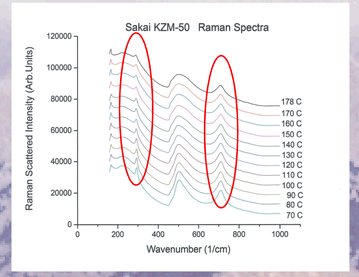
Raman Spectroscopy

500 nm Sakai BTO



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

50 nm Sakai BTO



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

Acknowledgments

Prof. Charles Taylor (Pomona College)
Prof. Robert Gaines (Pomona College)
Prof. David Tanenbaum (Pomona College)
Prof. Ronald Grimm (Harvey Mudd College)
Tetsuya Ohtani (Sakai Chemical)

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. Use of the National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886. The DND-CAT located at the Advanced Photon Source (APS) is supported by E. I. DuPont de Nemours & Co., The Dow Chemical Co., and the State of Illinois. Use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract DE-AC02-06CH11357.