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Ferroelectric and Ferromagnetic Nanoparticles for High Energy and Power Density Applications

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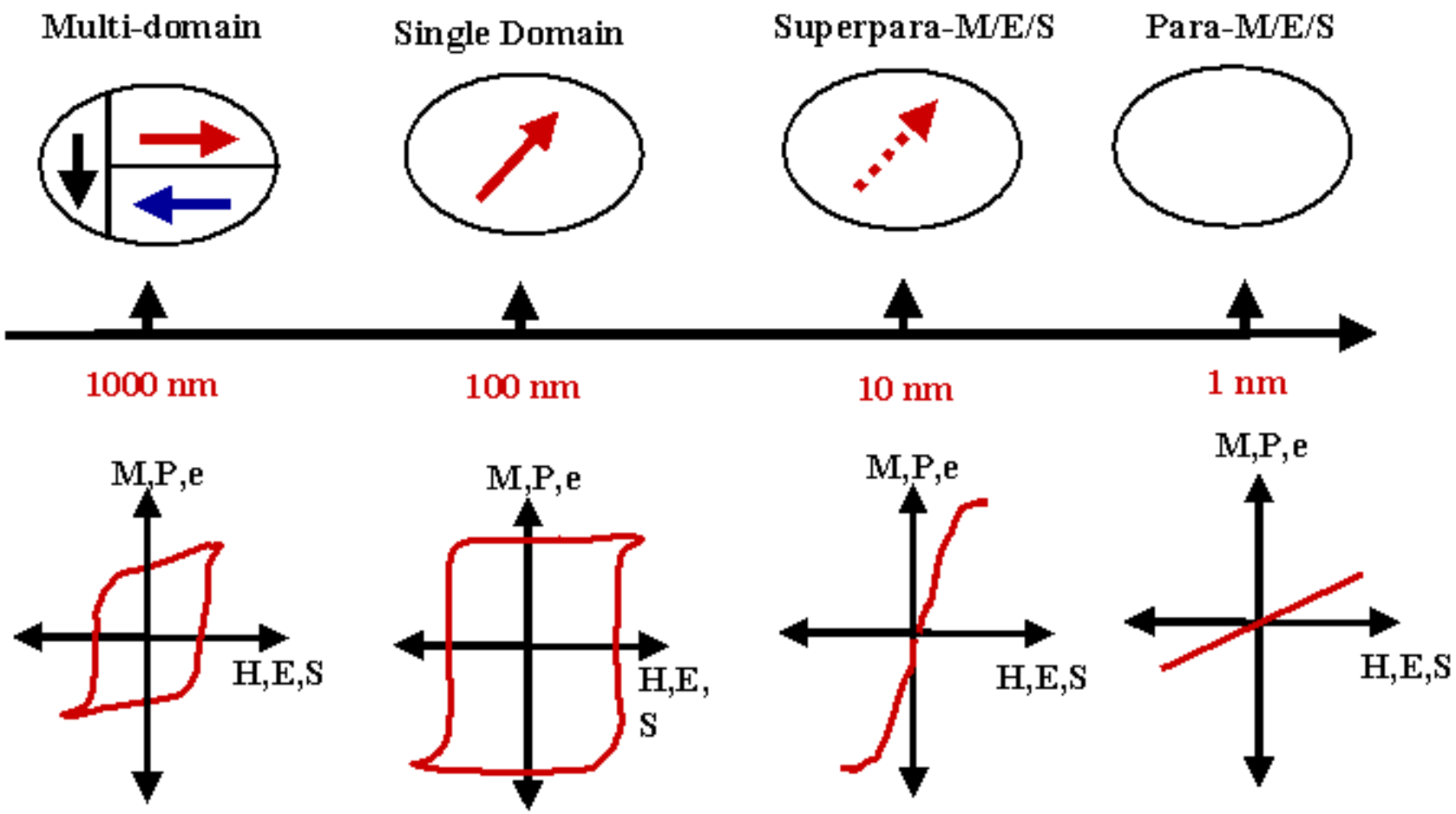
SIZE EFFECTS IN FERROICS (R. E. Newnham, 1992)



Transitions expected in *Ferromagnetics*, *Ferroelectrics* and *Ferroelastics* as a function of size.....

http://www.rci.rutgers.edu/~ecerg/pp_pres/eka1PHD/sld004.htm

Ferroelectric Nanoparticles

Benefits of Nanocrystalline Dielectrics

Nanocrystalline ceramics show much higher breakdown strength (BDS) compared to coarse grain ceramics ➔ higher energy density

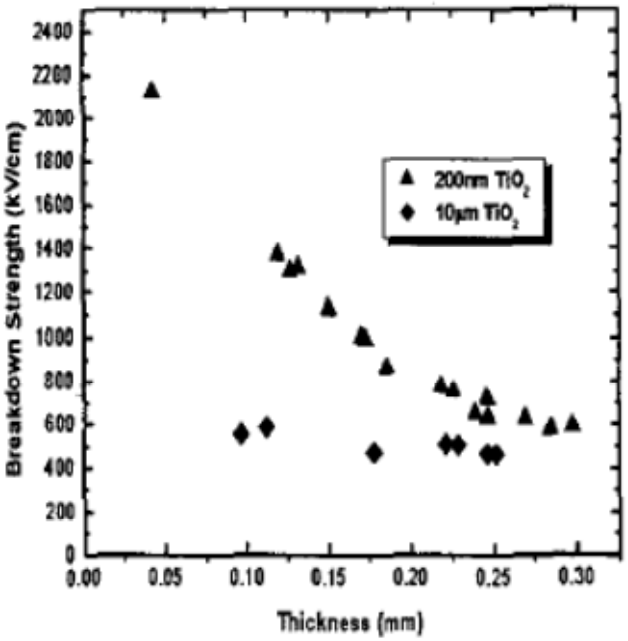


Figure 5. BDS as a function of dielectric thickness for nanocrystalline- and coarse-grained TiO_2.

Ye et. al., "Influence of nanocrystalline grain size on the breakdown strength of ceramic dielectrics", 2003

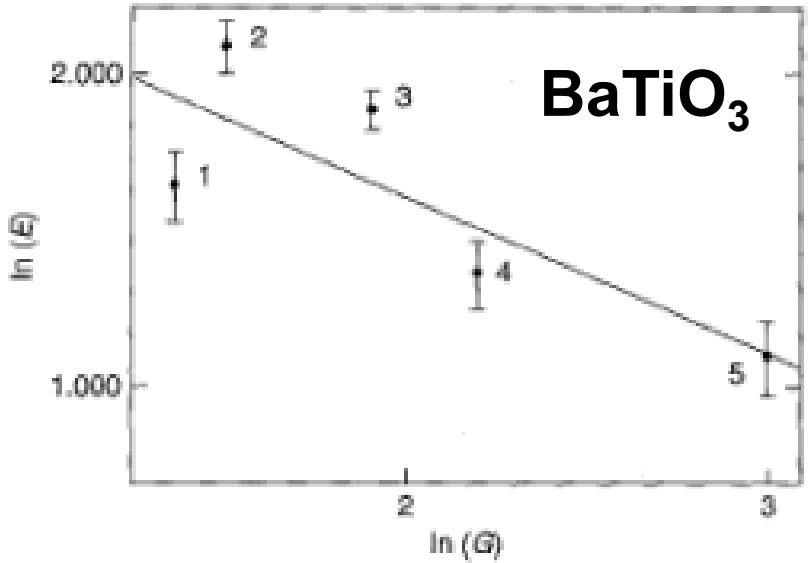


Figure 2 Grain size dependence on dielectric strength. Numbers indicate sintering temperatures: (1) 1320 °C, (2) 1330 °C, (3) 1350 °C, (4) 1380 °C, (5) 1400 °C.

Tunkasiri and Rujijanaul, J. Mater. Sci. Lett. **15** 1767 (1996)

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Benefits of Nanocrystalline Ferroelectrics

- For ferroelectric (FE) dielectrics, there are additional benefits:
  - Permittivity increases with decreasing grain size down to a critical size dimension (higher energy density)
  - High frequency performance improves with decreasing grain size (maintain permittivity and low loss to higher frequencies)
  - Field dependence of permittivity may improve (i.e. lower voltage coefficient of capacitance or VCC)

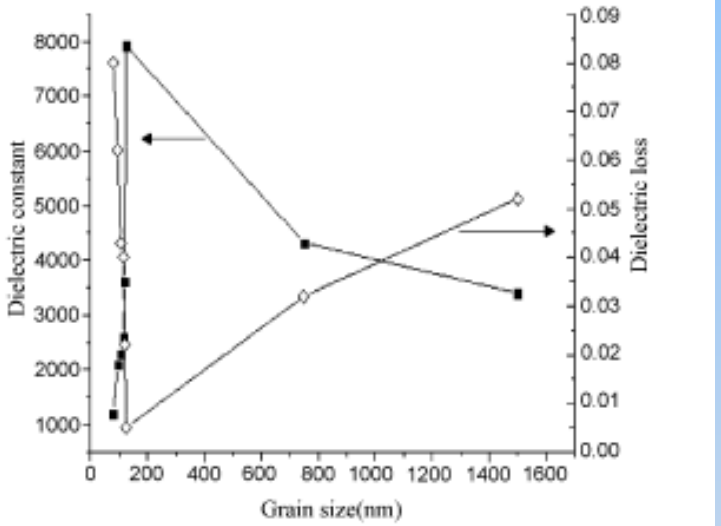

Fig. 7. 1 kHz dielectric constant and dielectric loss vs. grain sizes of nano-$BaTiO_3$ sintered at 1100 °C.

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

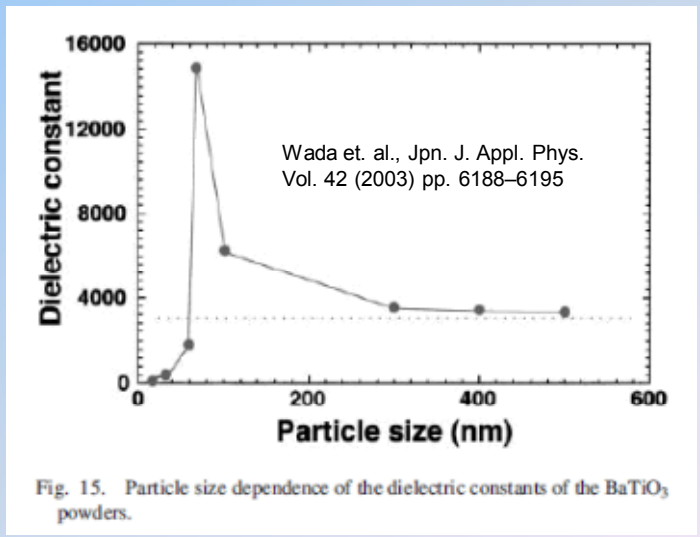

Fig. 15. Particle size dependence of the dielectric constants of the $BaTiO_3$ powders.

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Benefits of Nanocrystalline Ferroelectrics

- Nano-scale grains lose long range ordering
- Reduce lattice coupling and hence reduce strain ➔
- Better electromechanical performance and increased shot life

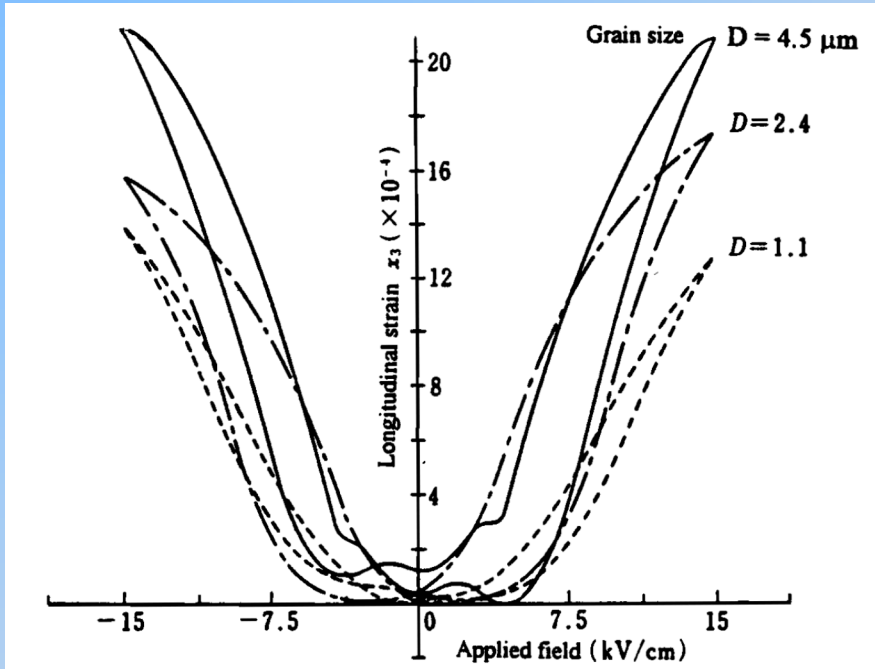

Fig. 3.28 Grain size dependence of the induced strain in PLZT ceramics.

from Kenji Uchino's book, Ferroelectric Devices

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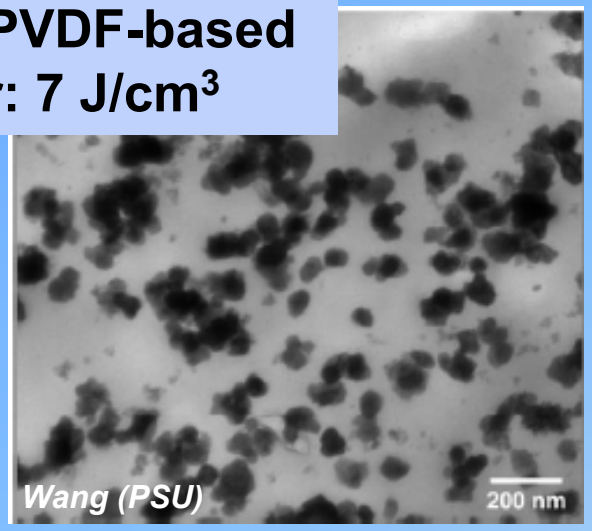
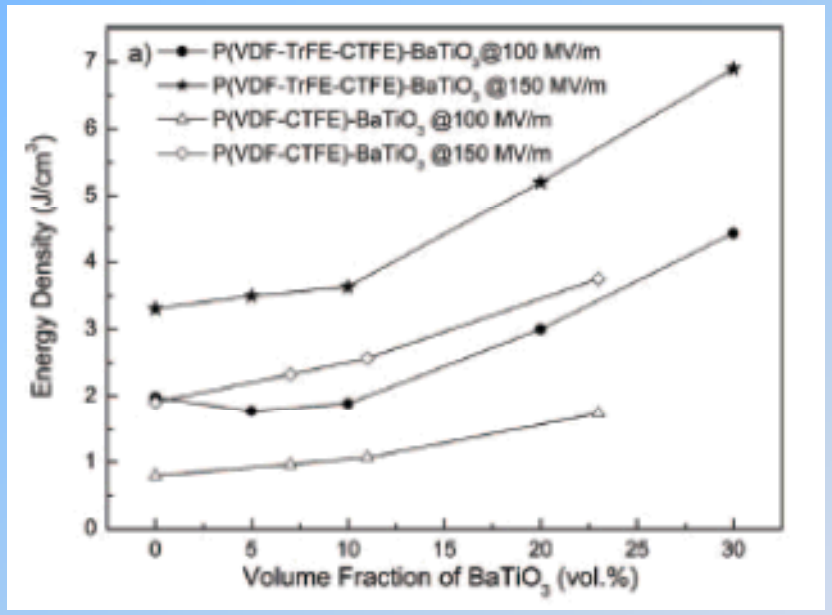
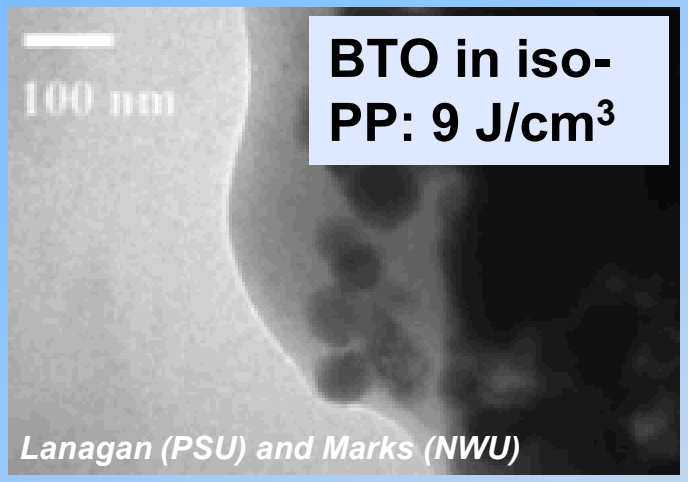
Polymer-Based Nanocomposite Dielectric Films

BTO in PVDF-based polymer: 7 J/cm^3







BTO in iso-PP: 9 J/cm^3

- **High energy densities demonstrated, but proof of performance in devices is lacking**
- **Low volumetric fraction of the inorganic particles (~ 25-30% loading)**
- **Size effects in ferroics not exploited**

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Ceramic/Glass Nanocomposite Solution

- Greater energy density through higher volumetric loading of the high permittivity dielectric
  - Glass based nanocomposite matrix provides a method for obtaining >90% loading of the nanoceramic ➔ higher energy density

Volume mixing law: $\log \varepsilon = v_1 \times \log \varepsilon_1 + v_2 \times \log \varepsilon_2$

Energy Density: $EnergyDensity = \frac{1}{2}\varepsilon_0 \varepsilon_r E^2$

- Glass matrix should provide better thermal stability than polymer materials for improved TCC (Temperature Coefficient of Capacitance)
- Glass phase has been shown to improve electromechanical reliability (higher BDS & shot life)
  - Composite structure can support electric fields well in excess of 500 V/mil
- More robust devices

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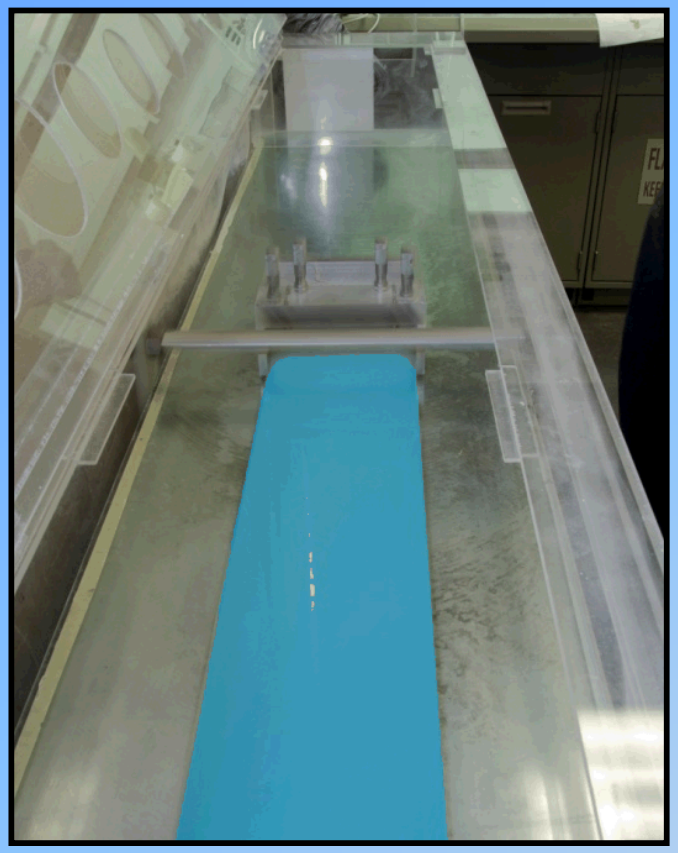
Integration into Multilayer Configuration



- The technology for fabricating multilayer polymer-based nanocomposite capacitors for pulsed energy applications is not mature
- This effort uses ceramic tape casting routes for casting, laminating, and firing multilayer parts

Lab-scale tape casting setup at SNL

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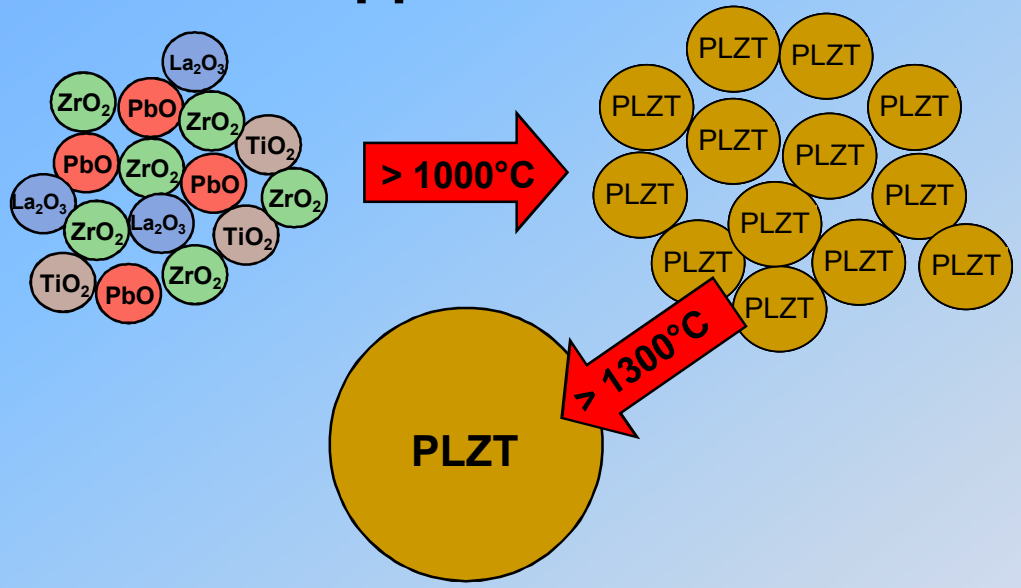
Materials Approach

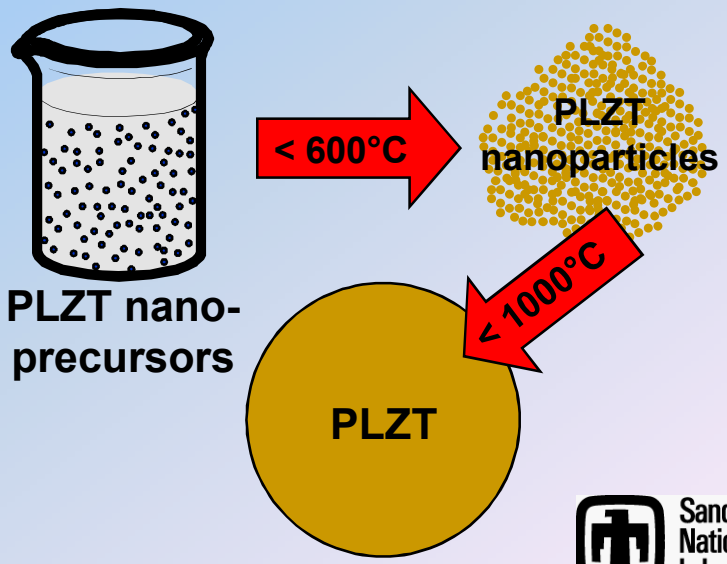
Approach:

- Synthesize nanoscale precursors for ceramic capacitors using room temperature solution based chemistry
- Develop sintering profile for nanoscale precursors and incorporate grain growth inhibitors and/or sintering aids to decrease firing temperature further and improve device performance

Traditional approach:



Our approach:



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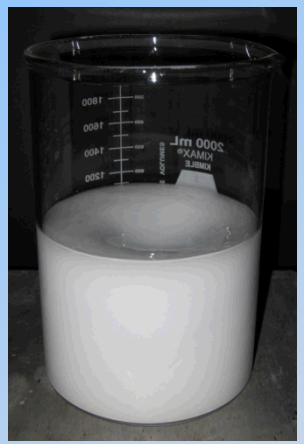
PLZT

PLZT Scaleable Aqueous Synthesis Route

- $Pb(NO_3)_2$, $ZrO(NO_3)_2$ & La_2O_3 dissolved in HNO_3
- Diluted $Ti(OPr)_4$



- Ammonium hydroxide to rapidly raise the pH

- Wash, centrifuge, and filter precipitate

- Dry amorphous precipitate with large surface area

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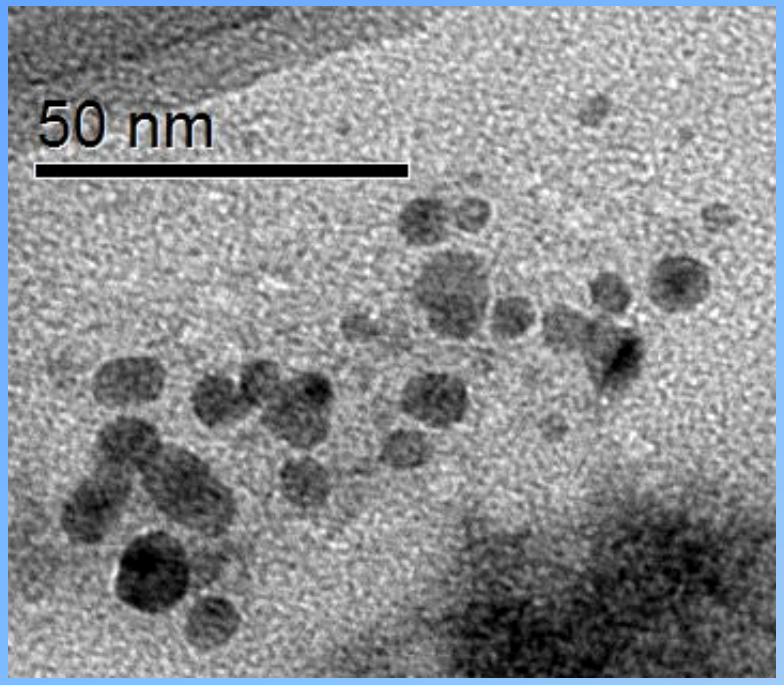
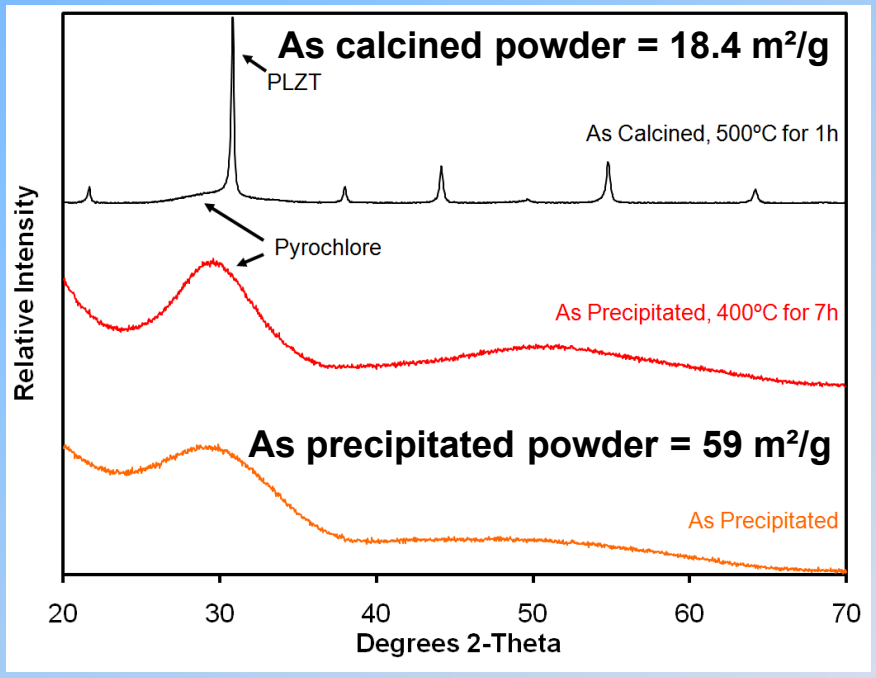
PLZT Nanoparticle Based Capacitors





- **Significant lowering of calcining temperature (300 – 500 ˚C)**
- **Crystallite size is reliably <100 nm but the dry powder is agglomerated**

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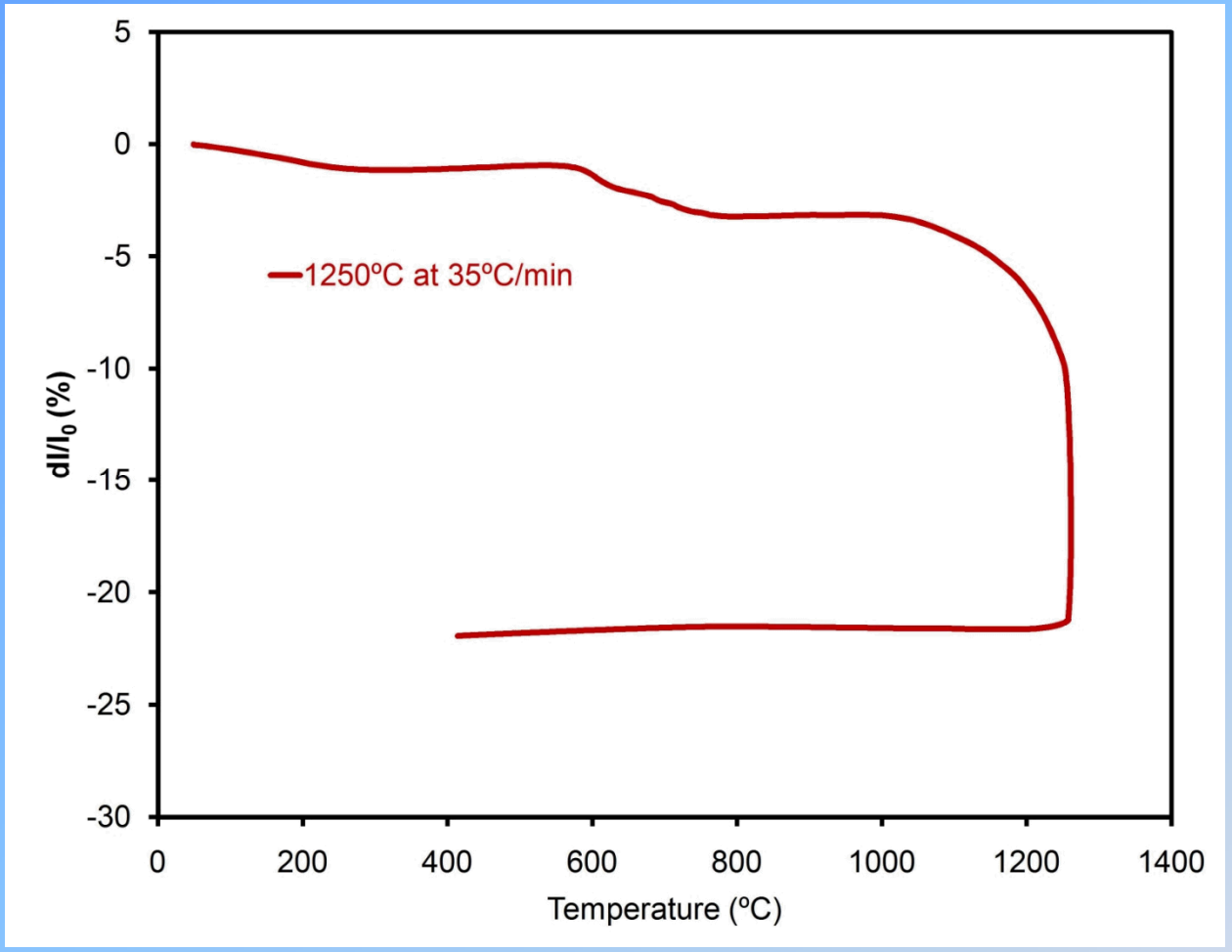
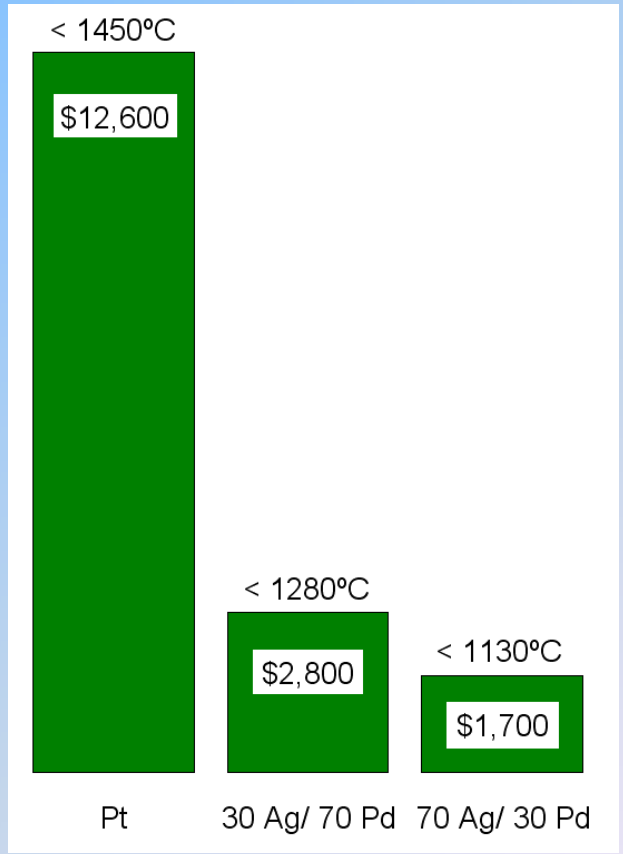
Lowered Sintering Temperature





- **> 4-fold decrease in electrode cost transitioning from Pt to 70/30 Ag/Pd**
- **Reduced lead volatility**

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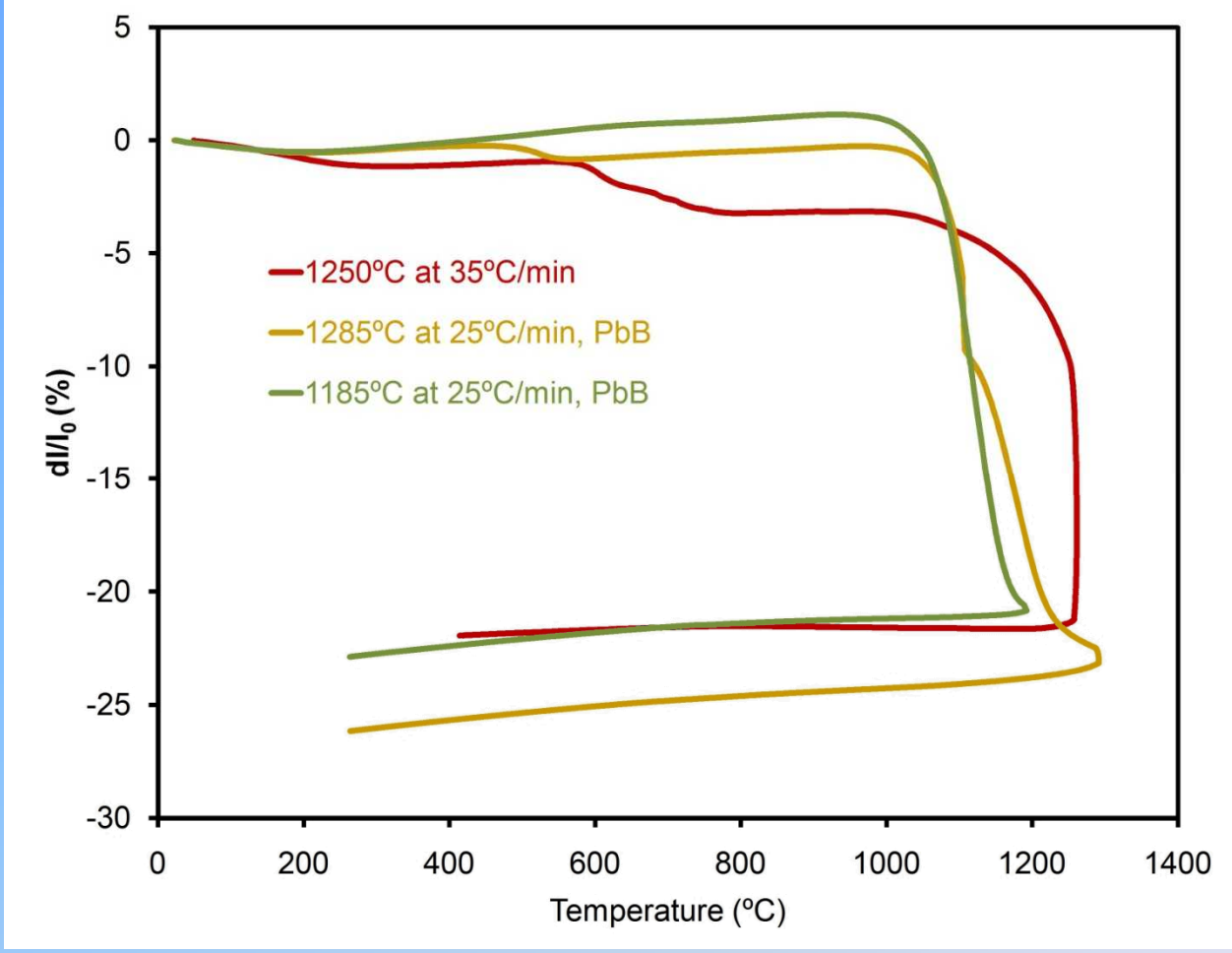
Glass Sintering Aids



- **0.5 w/w loading**
- **Need to ensure glass does not detract from electrical properties**

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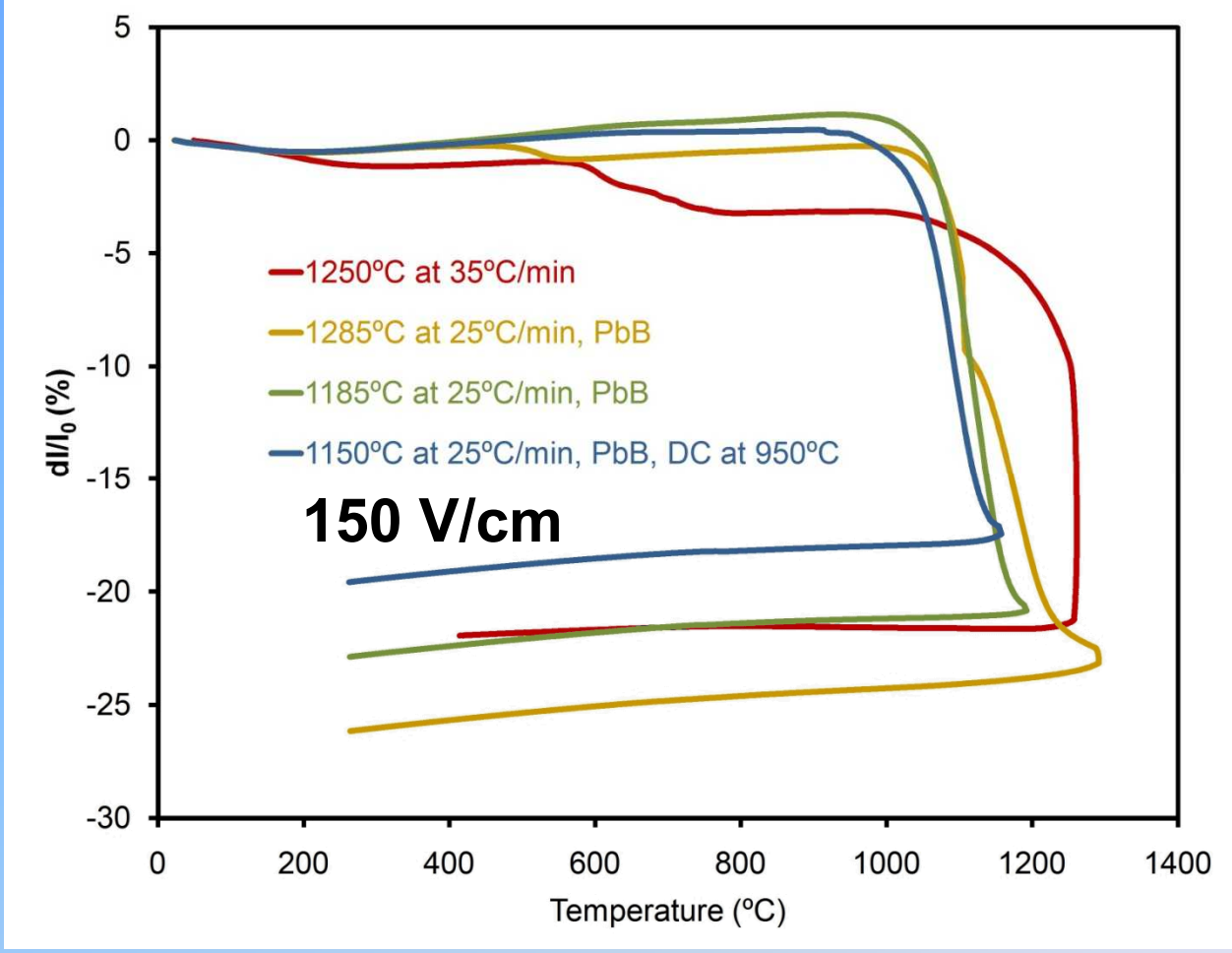
Electric Field Assisted Sintering



- Higher electric fields may result in even lower sintering
- Temperatures similar to spark plasma sintering

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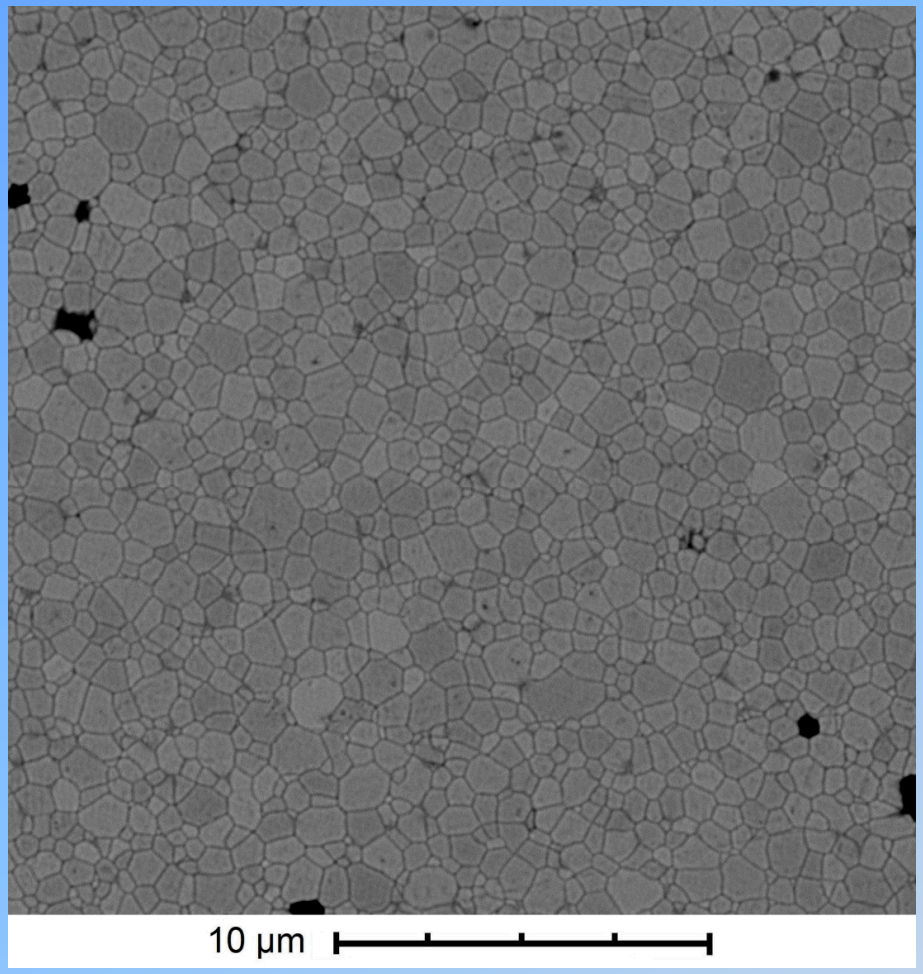
SEM of Sintered PLZT

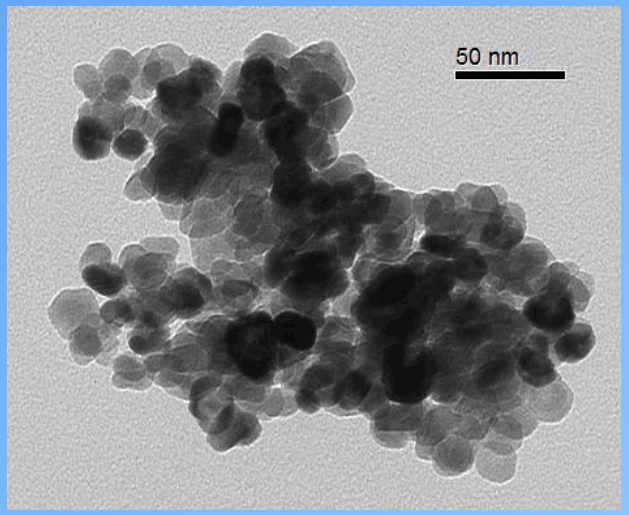


- Sintered with glass aid
- No field assist
- Good densification
- Some grain growth
- Possible grain pull-out during polishing

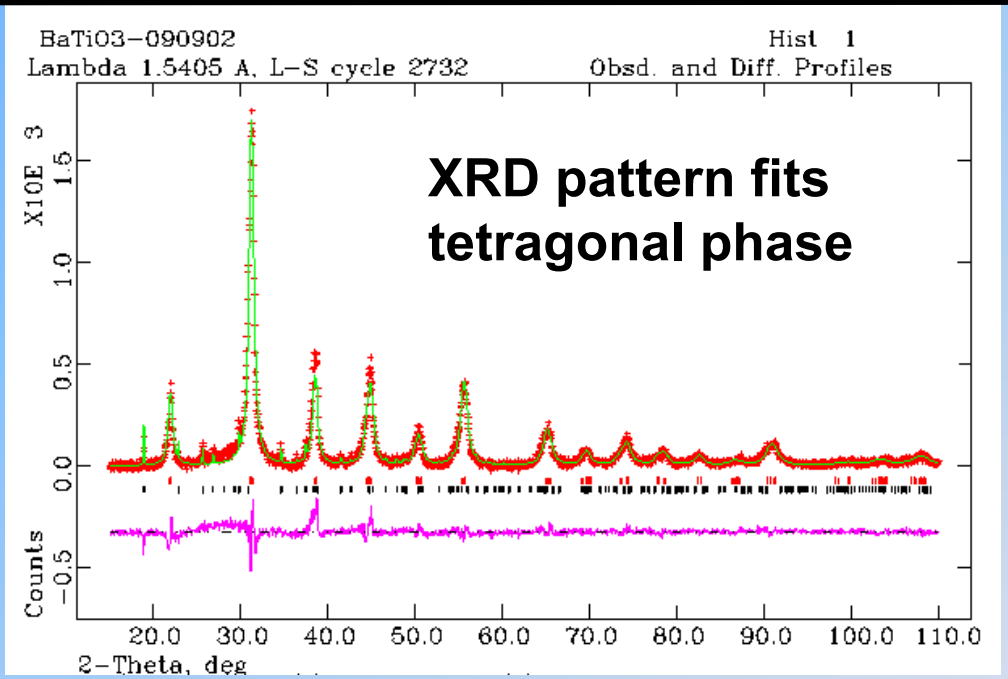
- All grains are < 2µm with many sub-micron grains
- Electric field may assist densification with smaller grain sizes

BTO

$BaTiO_3$ Nanoparticle Synthesis, $Ba(OH)_2 \cdot 8H_2O$ Reagent



~ 10 nm diameter



- $Ba(OH)_2 \cdot 8H_2O$ and $Ti(OPr)_4$ precursors at 80 ˚C
- Redesigned synthesis using air-free chemistry and with improved control over water addition
- Modified synthesis for our dry environment through extra H_2O addition
- XRD indicates tetragonal phase present when particles synthesized with 0.5 and 0.6 mol H_2O

Yoon et. al., *J. Am. Ceram. Soc.* **90** 311 (2007)

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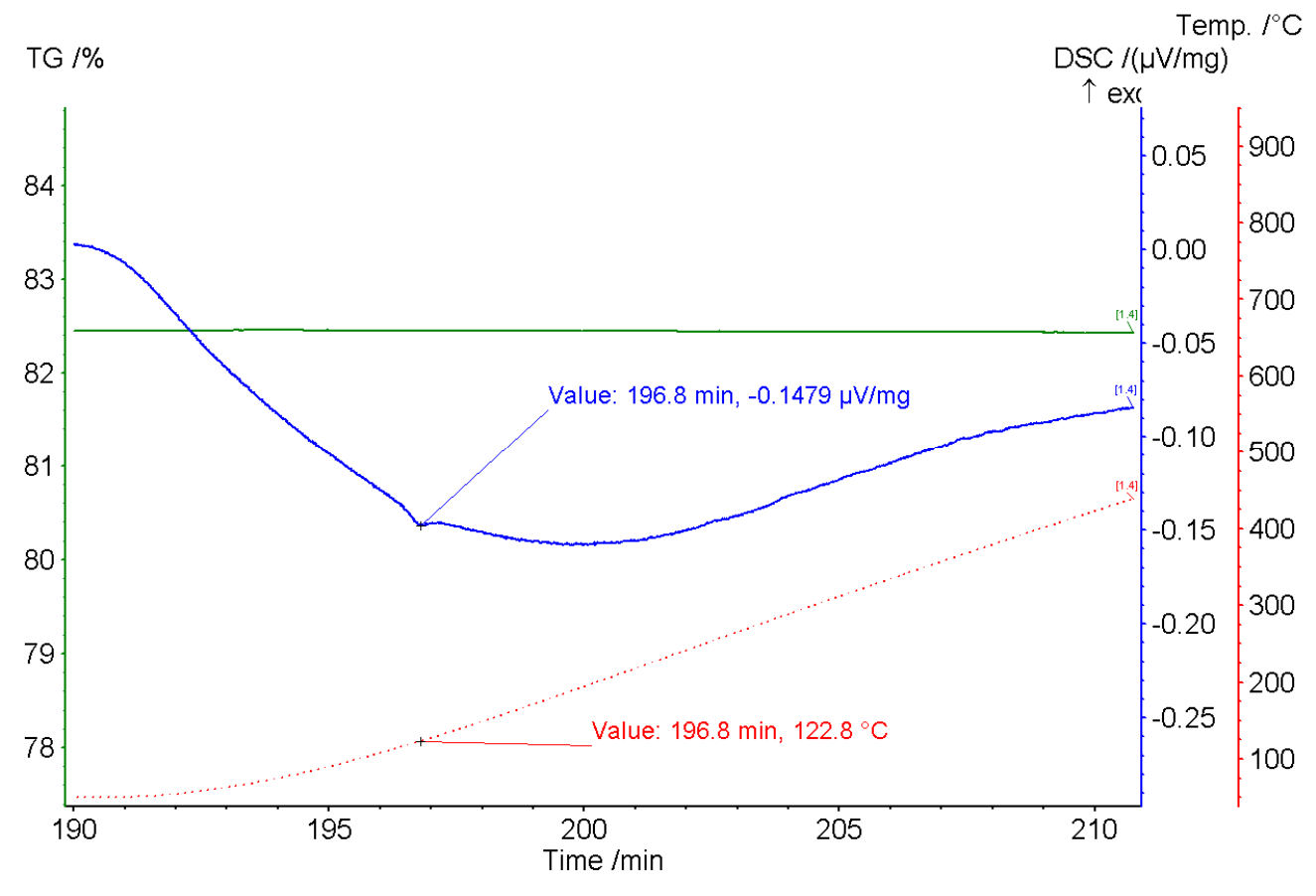
$BaTiO_3$ Nanoparticle Synthesis, $Ba(OH)_2 \cdot 8H_2O$ Reagent



- Reheated BTO particles after initial cycle to 1300 ˚C
- Endotherm at 122.8 ˚C consistent with BTO Curie temp. (tetragonal ➔ cubic phase transition)

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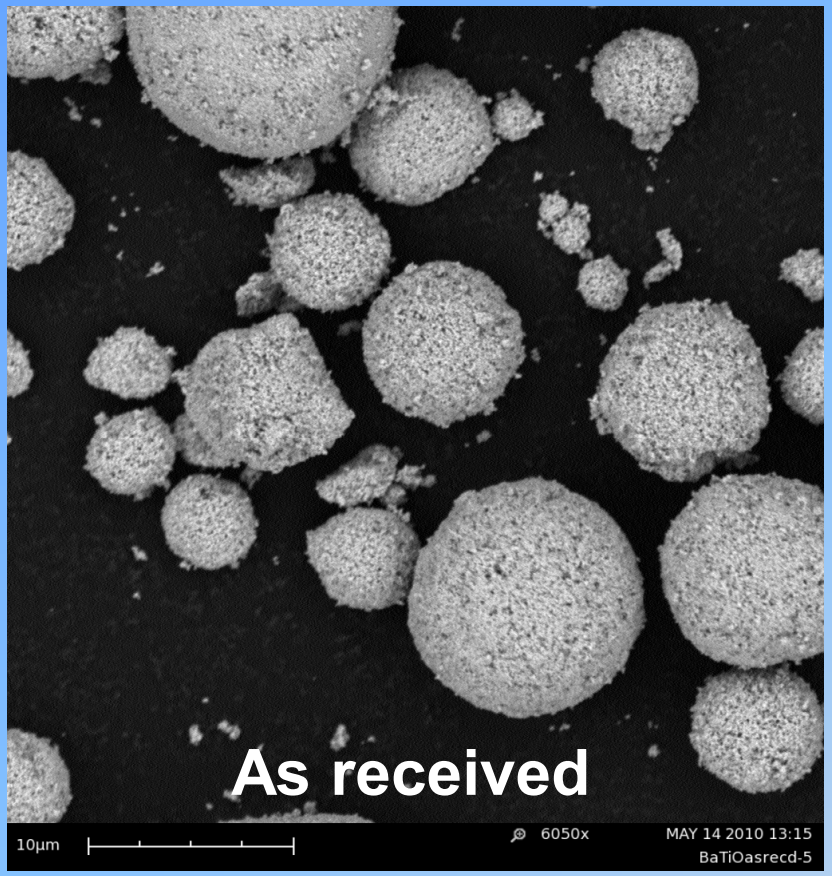
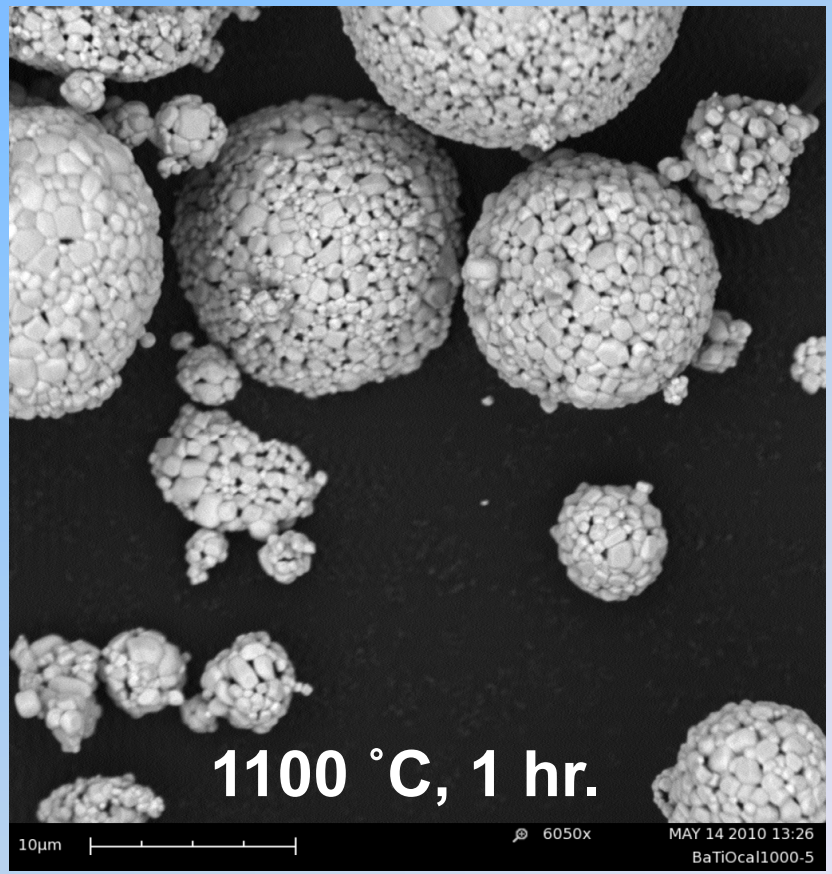
$BaTiO_3$ from TPL: SEM





- Primary particles of ~60 nm agglomerated into several micron clusters
- Coarsening of primary particles (~0.5 µm) with heating
- Breaking up agglomerates will improve homogeneity of composites

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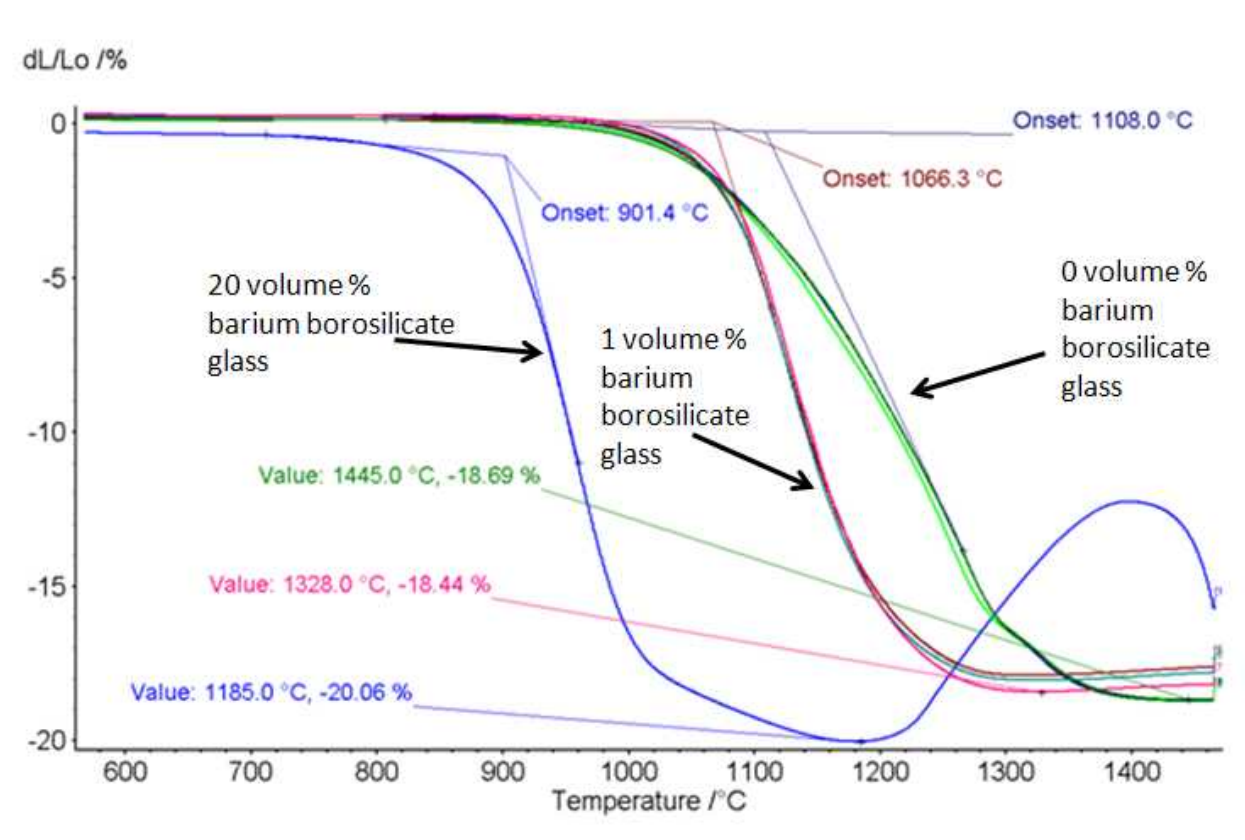
$BaTiO_3$ Nanocomposite Devices

Dilatometer sintering results



- Sintered TPL nano-BTO pellets from 0 - 20 vol% borosilicate glass loading
  - Sintering temp. reduced by almost 300°C through glass addition
  - Sample porosity also appears to decrease

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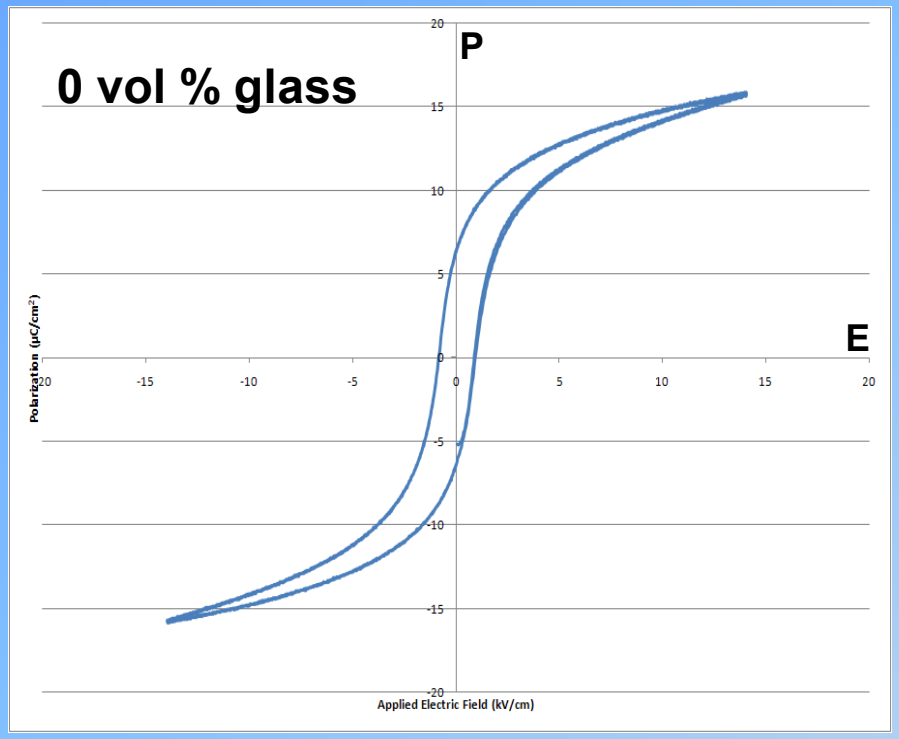
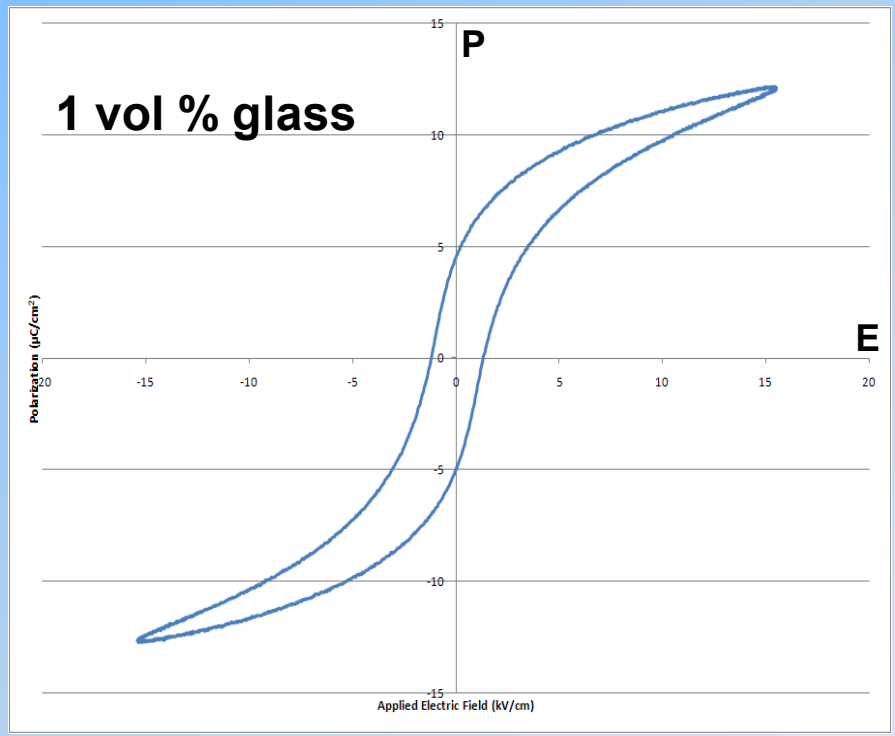
$BaTiO_3$ Nanocomposite High Field Hysteresis





- More open hysteresis loop with the addition of glass

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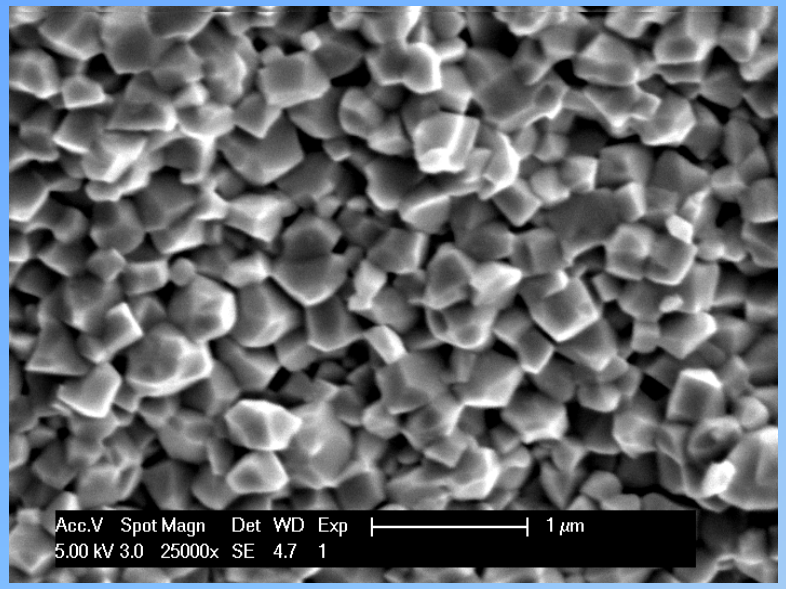
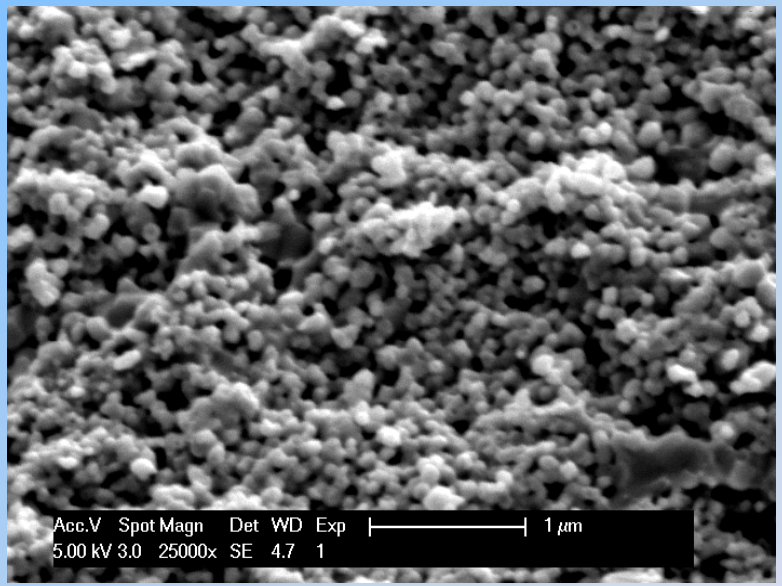
SEM of SPS BTO



TPL BTO, grain size 300 – 400 nm



SNL BTO, grain size 100 – 200 nm

- Spark Plasma Sintering (SPS)
- BTO powders pre-calcined
- SPS at 950 ˚C

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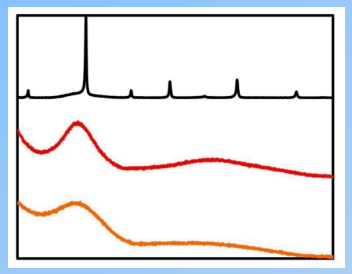
Conclusions - Ferroelectrics

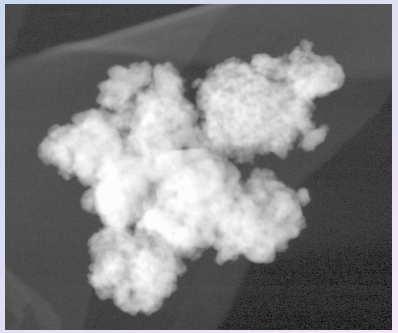
- **A scalable, environmentally benign synthesis route to generate nano-crystalline PLZT & BTO has been developed**
- **Several techniques to lower sintering temperature have proven effective and will assist fabrication of test devices**
- **Finding appropriate sintering aid amounts & chemistries + ideal sintering conditions (temperature, pressure, electric field, atmosphere) is crucial!**



Acknowledgments

Mark Rodriguez

(XRD data collection & analysis)



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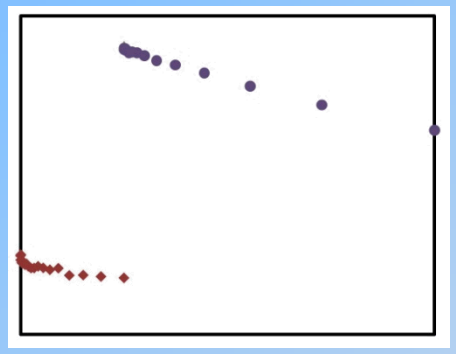
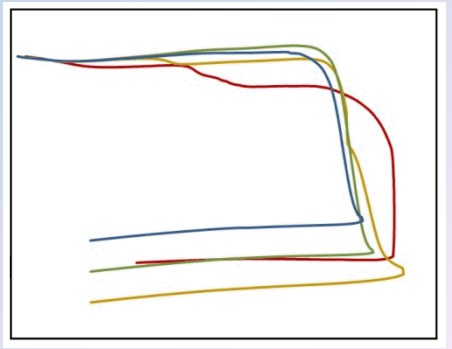
Future Work - Ferroelectrics

- Spray drying, thermal spray, and sonic dispersion (in combination with surfactants) will be examined to enhance particle dispersion
- Electric field assisted sintering and Spark Plasma Sintering (SPS) will be explored further
- More electrical results will be forthcoming
- All lessons learned processing PLZT will be applied to nano-BTO processing





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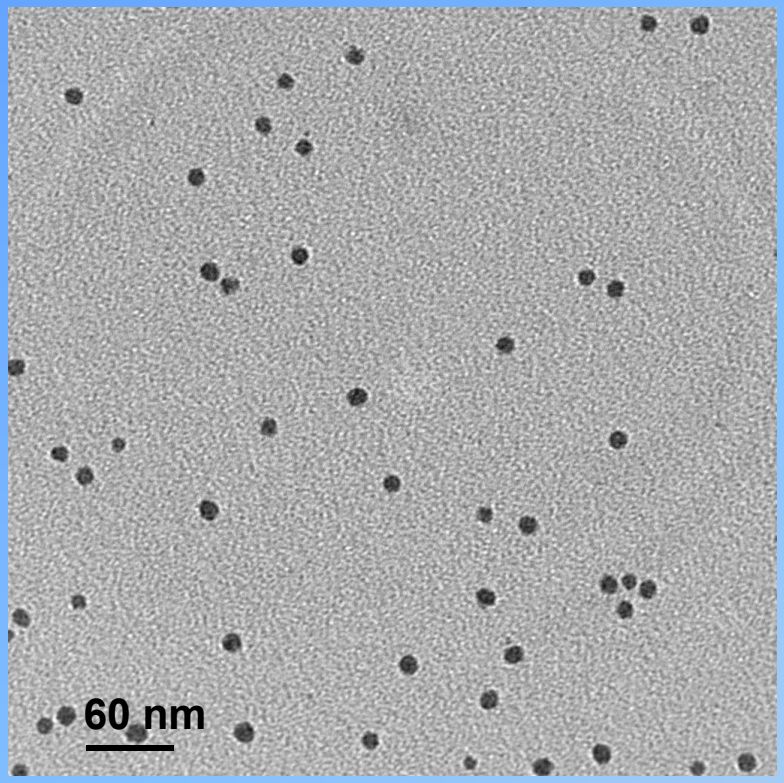
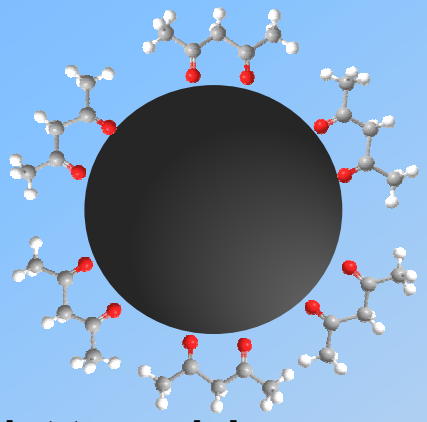
Ferromagnetic Nanoparticles

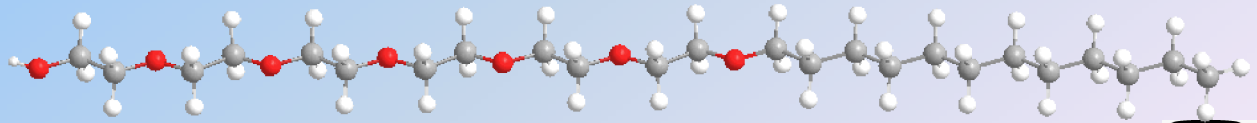
Fe Nanoparticles



- Thermal decomposition of iron pentacarbonyl in organic solvent
- Size control (2 — 10 nm diameter) through controlling ratio of iron pentacarbonyl to surfactant
- Synthesized with two surfactants: acetylacetone (2,4-pentanedione or PD) and hexaethylene glycol monododecylether (C12E6)
- Water and oxygen are carefully excluded through air free chemistry techniques



Not to scale!



Huber et al, *J Magn Magn Mat* **278,** 311 (2004)

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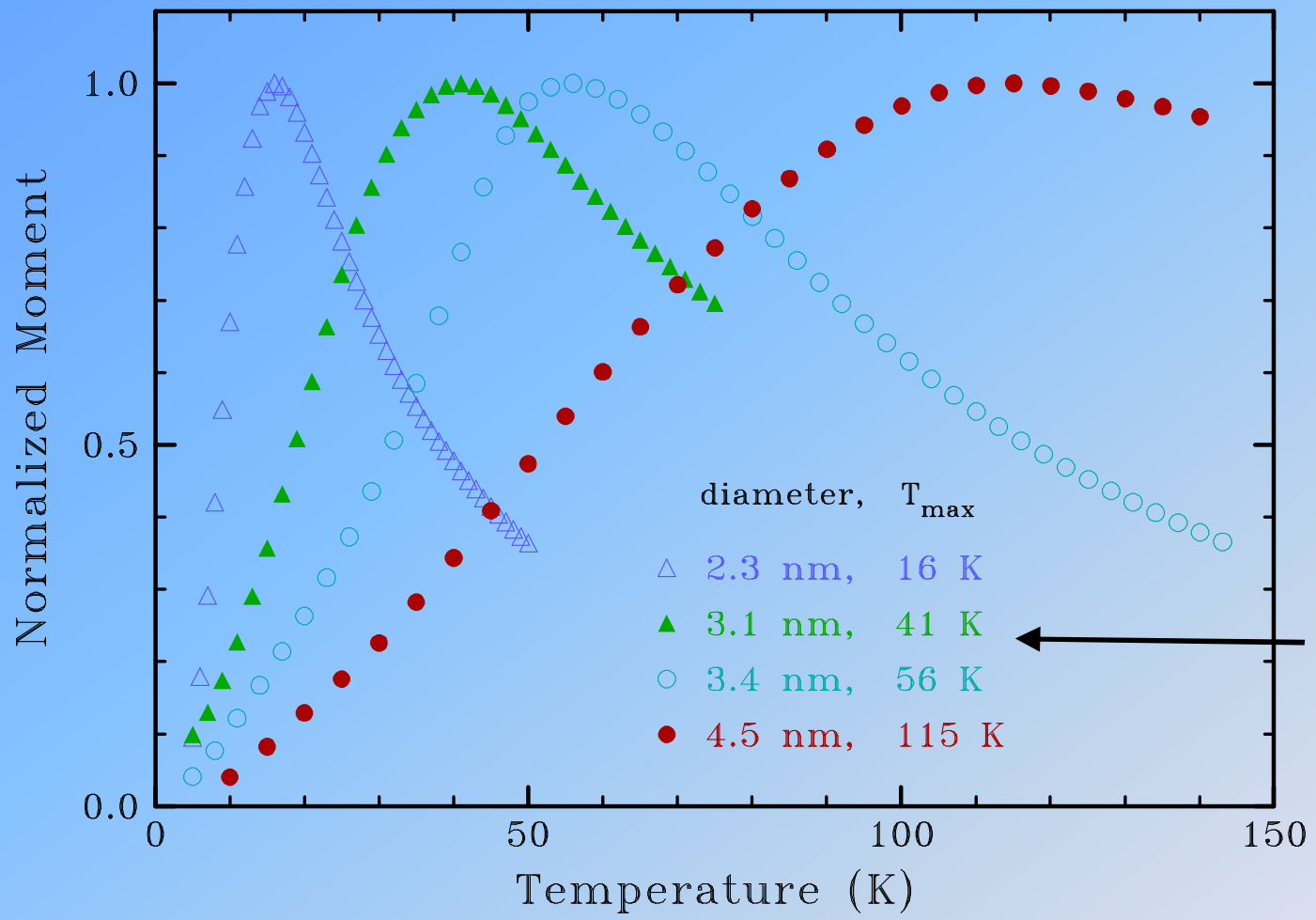
T_B vs. Fe Nanoparticle Diameter



T_B scales with V

- All curves ZFC
- Broad peaks for larger particles expected
- Plotting σ vs. T/T_B peaks would superimpose

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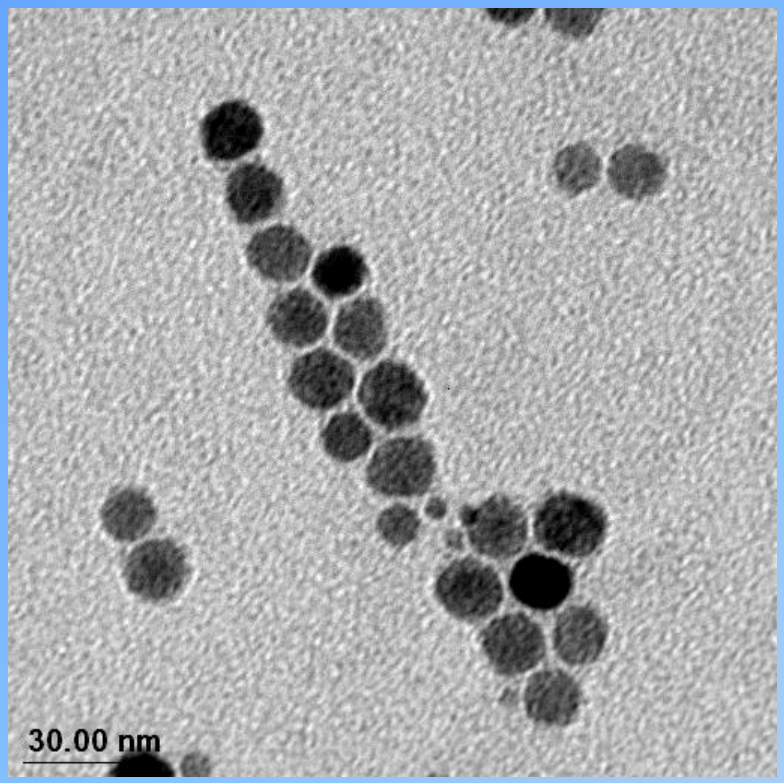
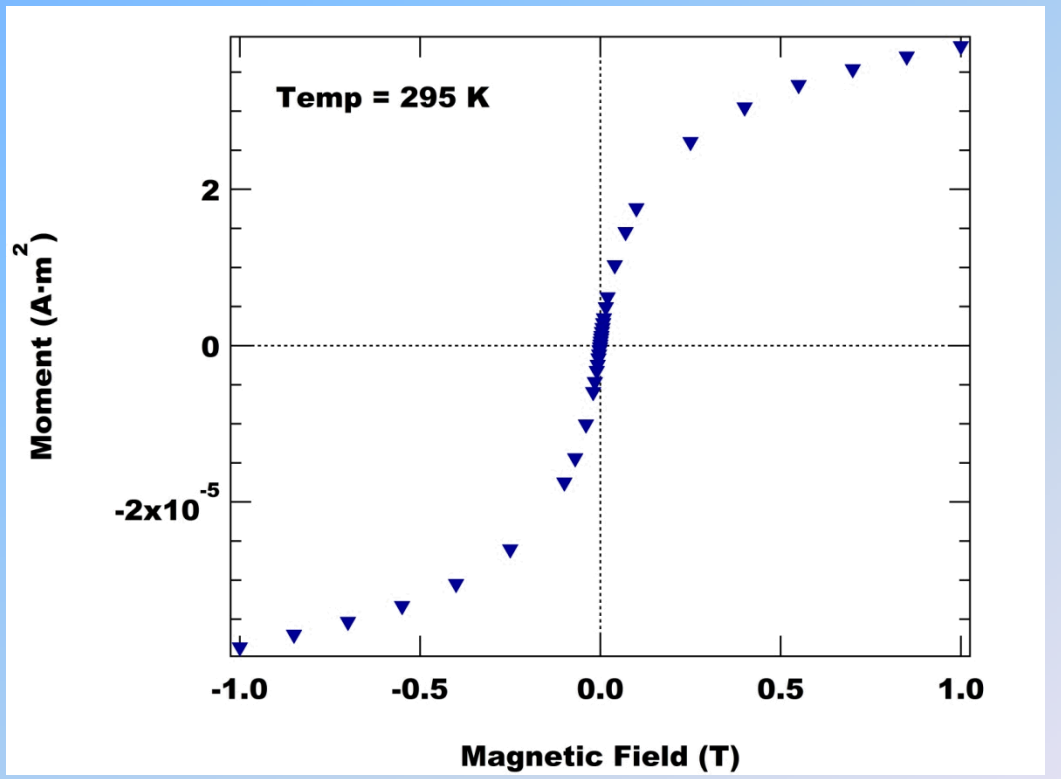
Fe_3O_4 Nanoparticles





- Fe_3O_4 Nanoparticles with poly(ethylene glycol) or PEG ligands
- Also possible to synthesize $Zn_xFe_{3-x}O_4$ and $Ni_xFe_{3-x}O_4$ nanoparticles (suitable for transformer core materials)

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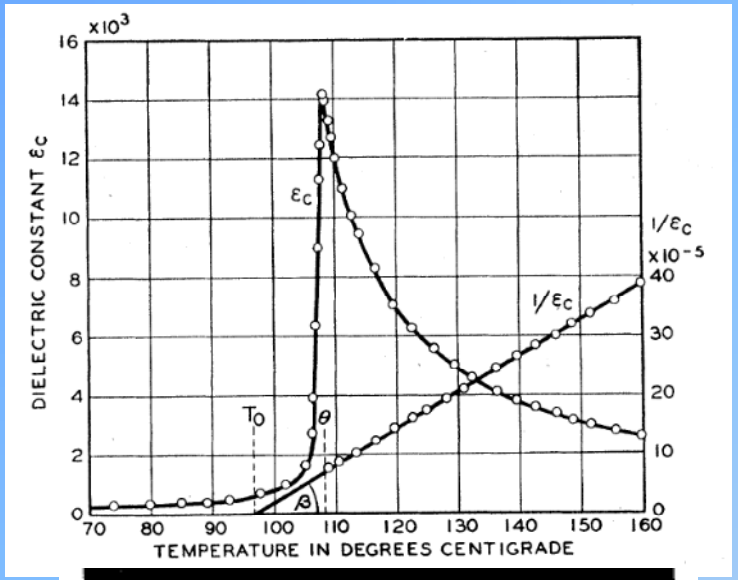
Extra Slides

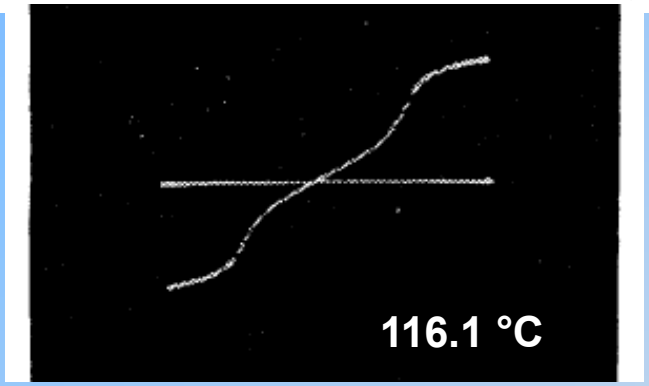
Project Motivation & Goals

- Form composites with high volumetric loading of ceramic nanoparticles in a glass matrix
  - Achieve energy densities of 10 J/cc in robust devices with long shot life
  - Glass matrix will limit grain growth to preserve beneficial nanoscale properties of ferroelectrics
  - Glass will increase device breakdown strength (BDS)
- Develop $BaTiO_3$ & PLZT nanoparticle syntheses that will maximize device performance
  - Provide precise control over particle size and phase → allowing exploitation of size effects in ferroics
  - Tailorability of ceramic surface functionality to minimize grain growth and agglomeration while maximizing dispersion

Exploiting Size Effects for High Energy Density Dielectrics

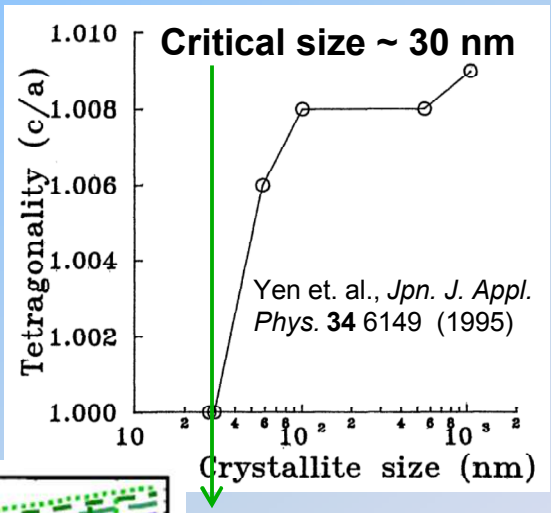
Paraelectric➔Ferroelectric (cubic➔tetragonal) phase transformations can be induced in ferroelectric materials that have lost their spontaneous polarization

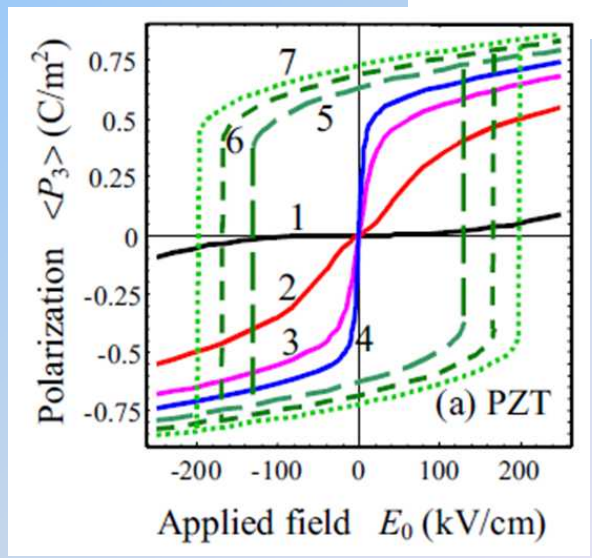




Merz, W. J., "Double hystersis loop of $BaTiO_3$ at the Curie Point", *Phys Rev* **91** 513 (1953)

$$KV \approx k_B T$$





Note: 1 through 7 are in order of increasing particle radius

M. D. Glinchuk, E. A. Eliseev, and A. N. Morozovska, "Superparaelectric phase in the ensemble of noninteracting ferroelectric nanoparticles", *Phys Rev B* 78, 134107 (2008)

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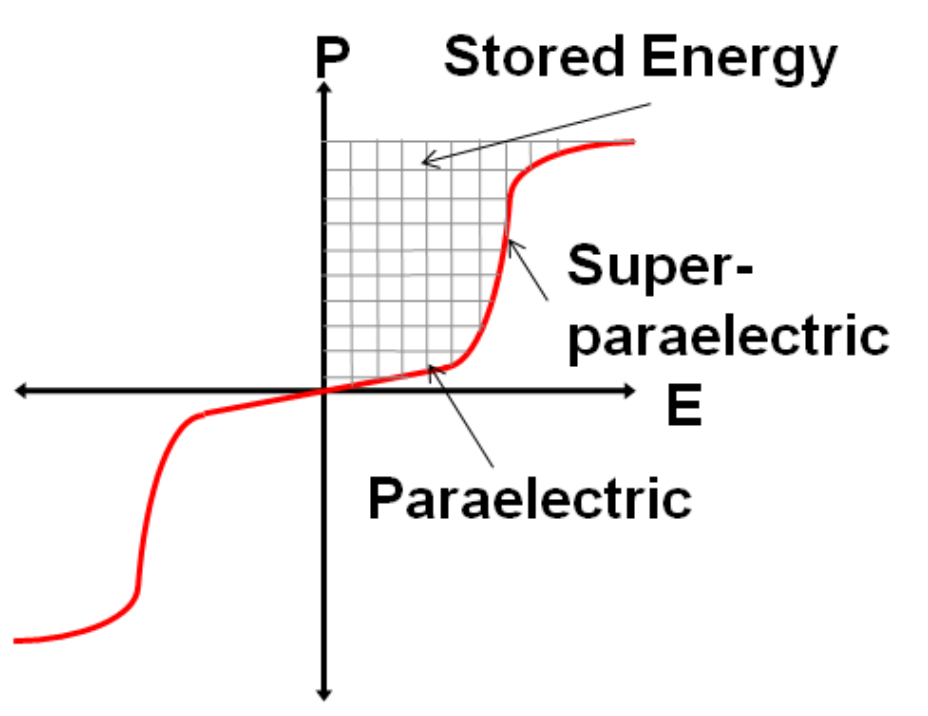
Increased Energy Density Through Phase Transformation

- Increased energy storage possible through field induced phase transformation
- Transition BTO from cubic (paraelectric) to tetragonal (ferroelectric)
- Device hysteresis will allow energy densities > 10 J/cc
- Nanoscale ferroelectric domains exhibit superparaelectric effect



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$BaTiO_3$ Results

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$BaTiO_3$ Nanoparticle Synthesis, Wada Synthesis Route

- **> 100 nm BTO particles synthesized via thermal decomposition of barium titanyl oxalate in atmosphere or vacuum**
- **Synthesized BTO precursor, barium titanyl oxalate, via aqueous route using $K_2TiO(C_2O_4)_2$ and $Ba(NO_3)_2$**

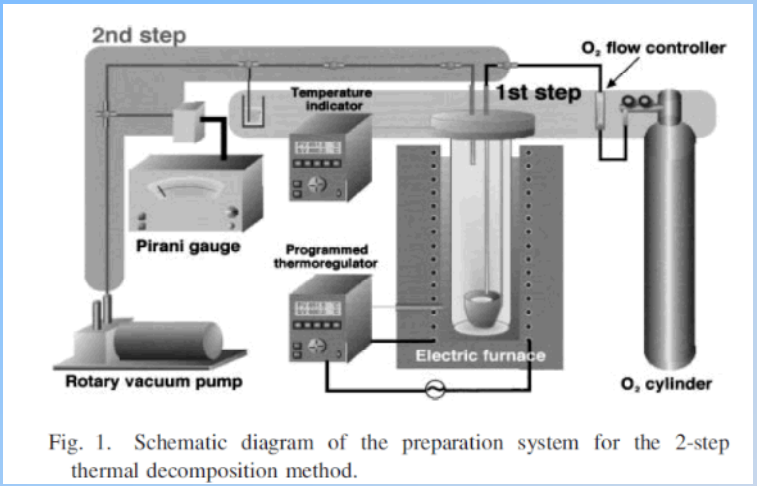
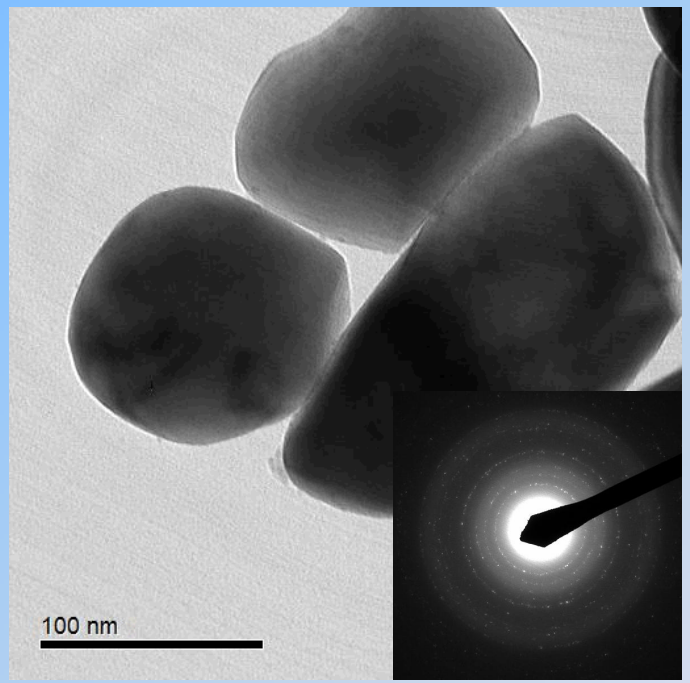


Fig. 1. Schematic diagram of the preparation system for the 2-step thermal decomposition method.



TEM image of BTO nanoparticles and SAED (inset)

Hoshina et. al., "Size and temperature induced phase transition behaviors of barium titanate nanoparticles," *J. Appl. Phys.* **99** 054311 (2006)

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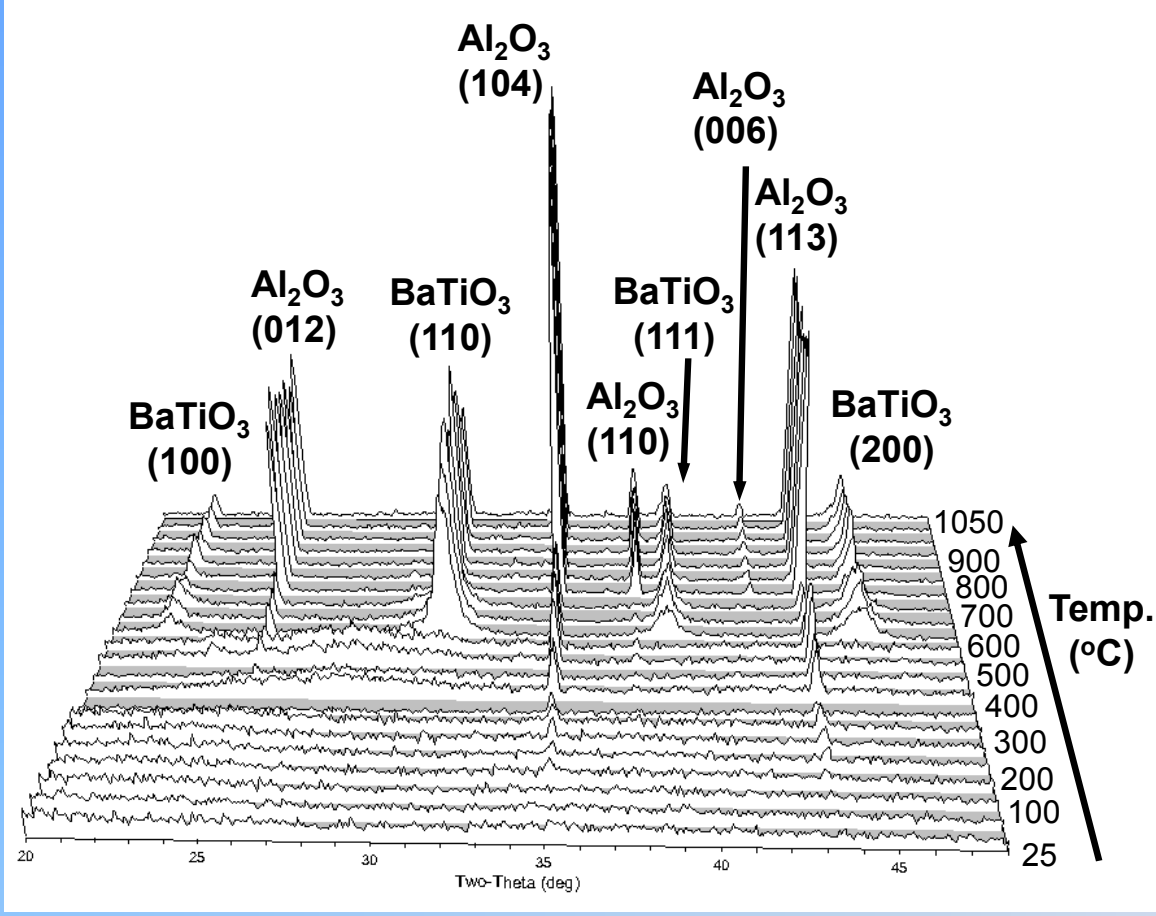
High temperature XRD of Barium Titanyl Oxalate



- Formation of strong amorphous pattern between 400 and 550 ˚C
- Crystallization of fine-grained $BaTiO_3$ at 600 ˚C, followed by further coarsening
- Al_2O_3 peaks appear at higher temperatures as the BTO powder consolidates and leaves the substrate area exposed

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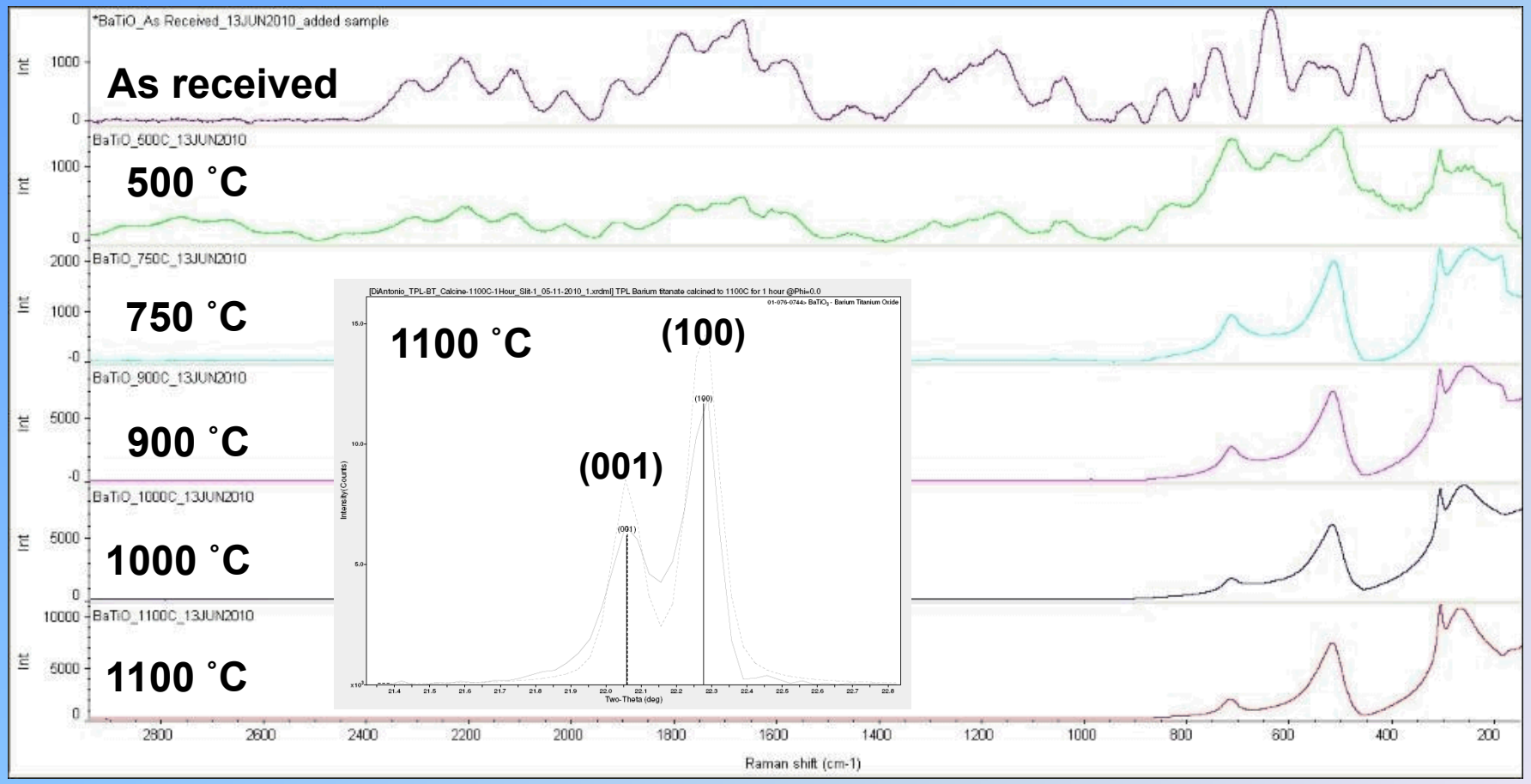
$BaTiO_3$ from TPL: Raman



- Raman indicates conversion to tetragonal phase begins at 500 ˚C
- Transition is complete at 800 ˚C
- XRD shows splitting of (001) and (100) peaks after 1100 ˚C

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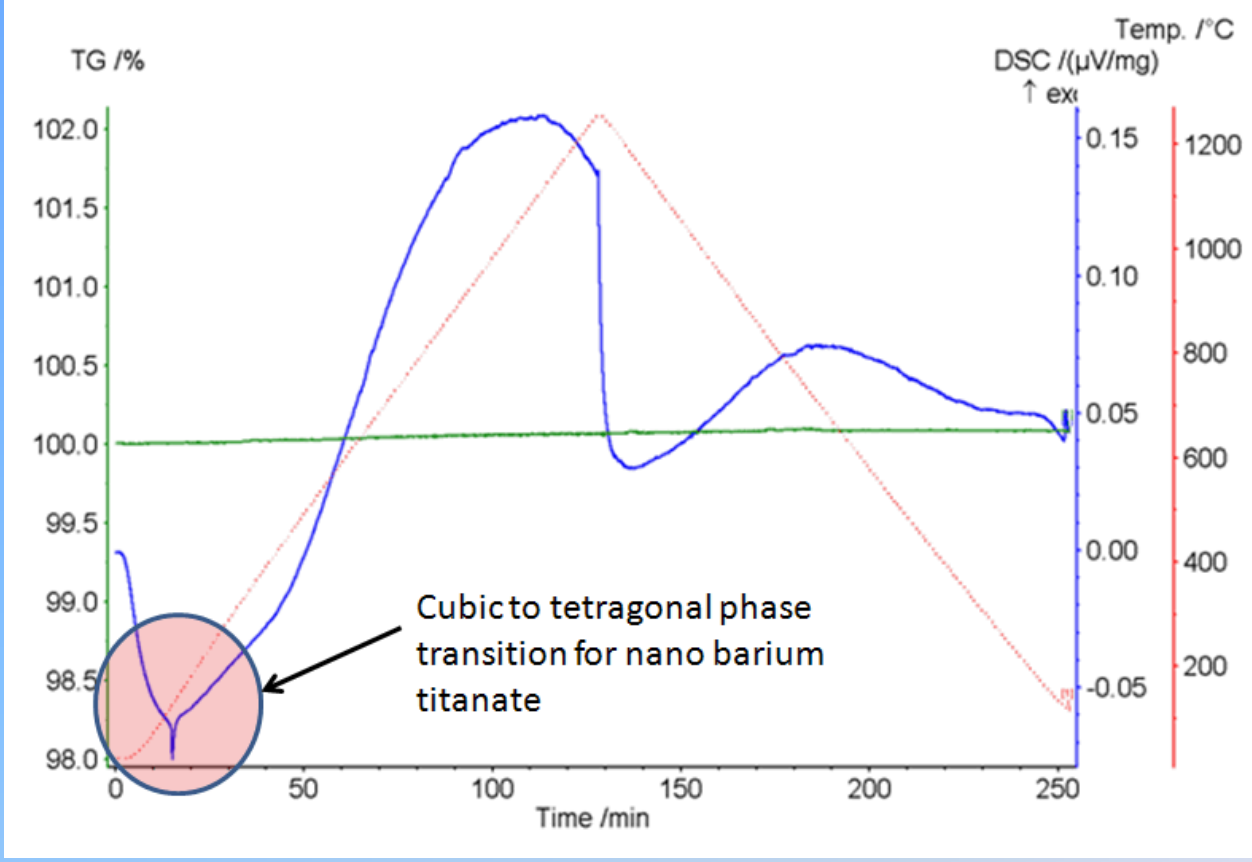
$BaTiO_3$ from TPL: STA



- **Simultaneous thermal analysis (STA)**
- **Tetragonal to cubic phase transition is apparent for calorimetric results (DSC or differential scanning calorimetry)**
  - **Phase transition only visible after heating to 1300°C**

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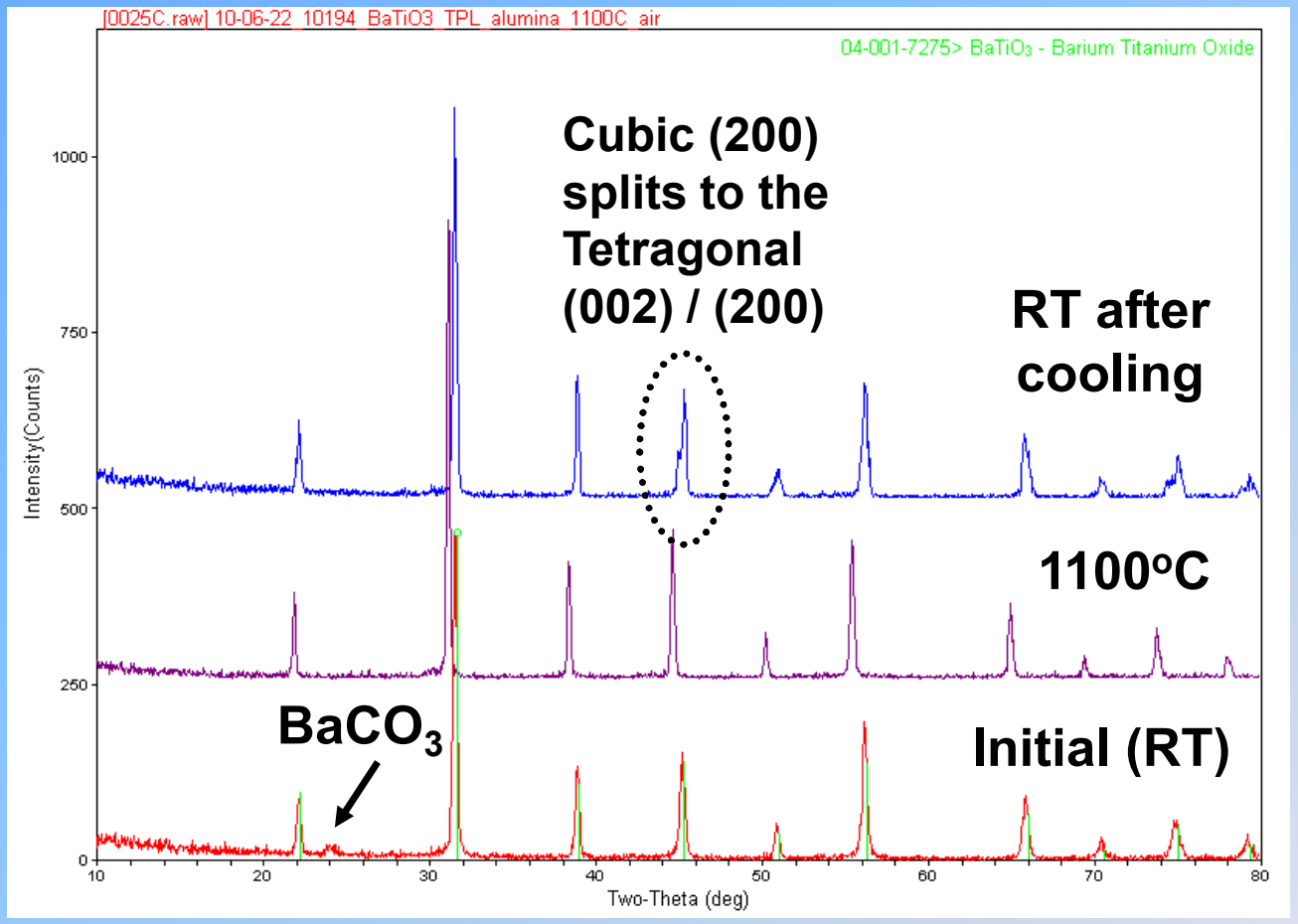
$BaTiO_3$ from TPL: High Temp. XRD



- TPL BTO shows an initial cubic structure
- peak sharpening of the cubic pattern at 1100 ˚C (grain growth)
- Tetragonal splitting of peaks upon cooling back to RT

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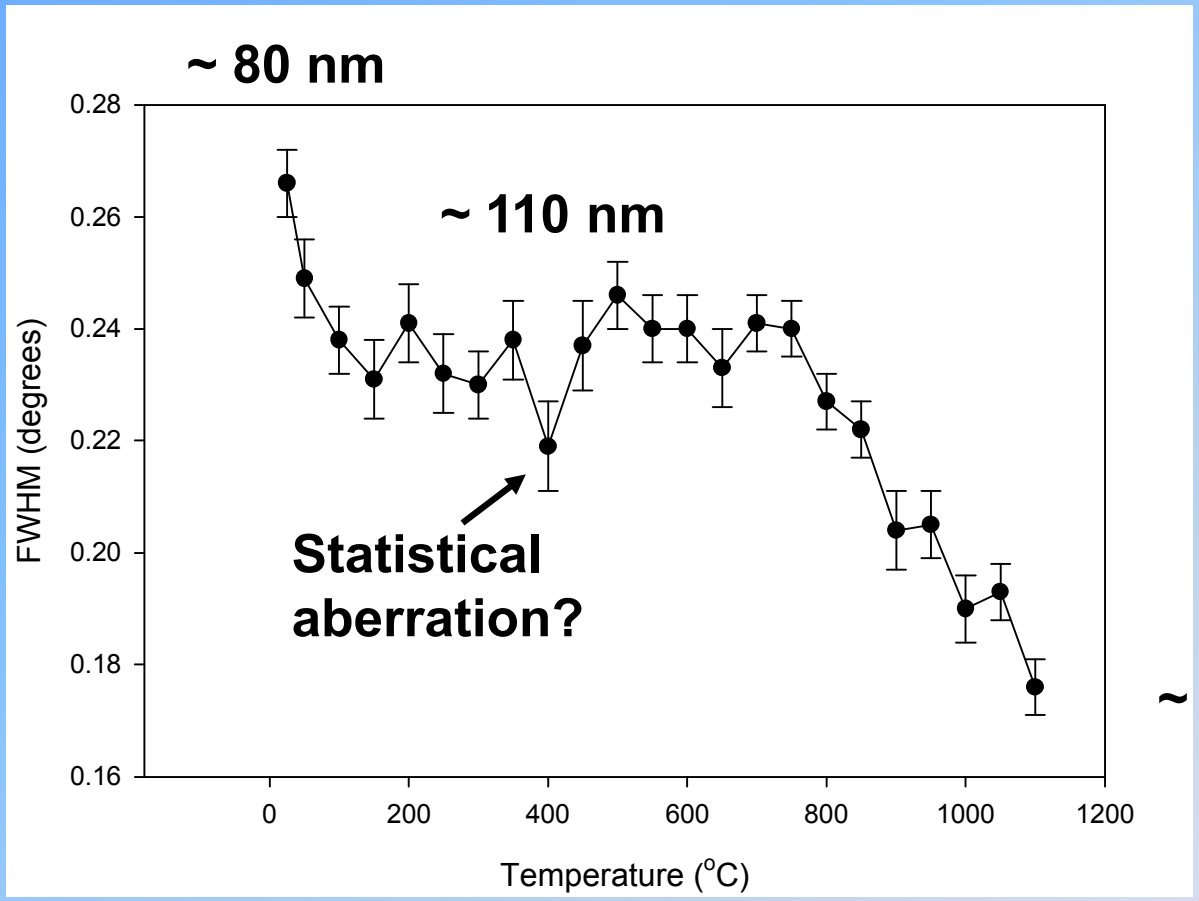
$BaTiO_3$ from TPL: High Temp XRD

$BaTiO_3$ (110)



~ 1 μm

- FWHM for (110) BTO 100% peak shows decease from RT to 150 ˚C
- FWHM levels off until ~800 ˚C
- Above ~800 ˚C we see another significant drop in FWHM

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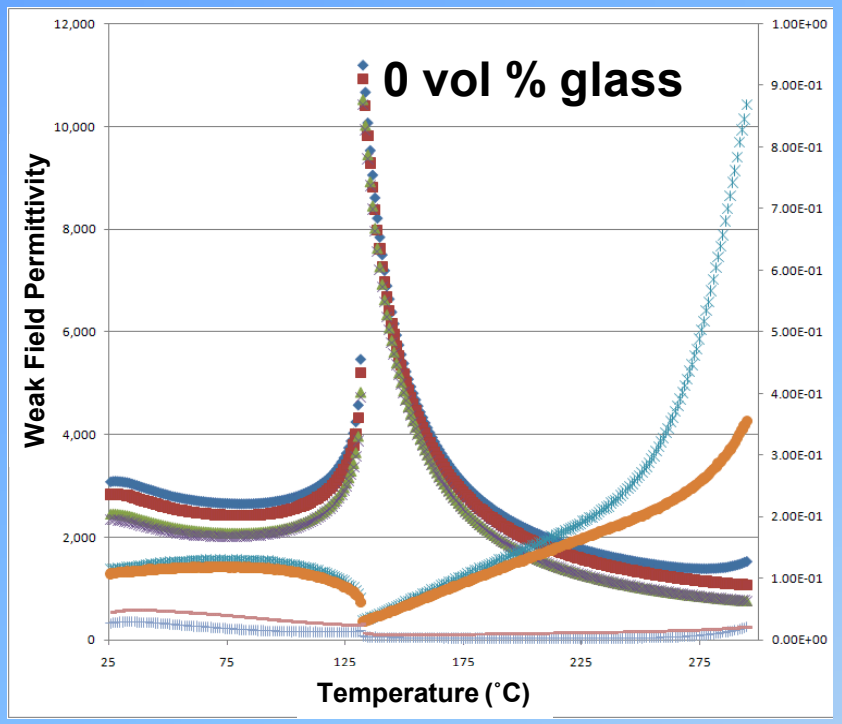
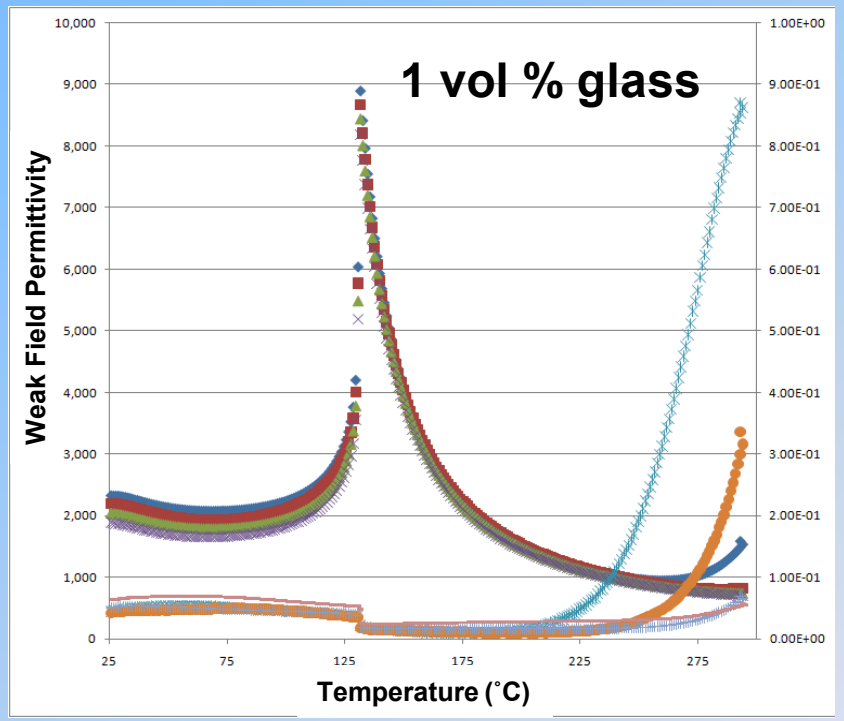
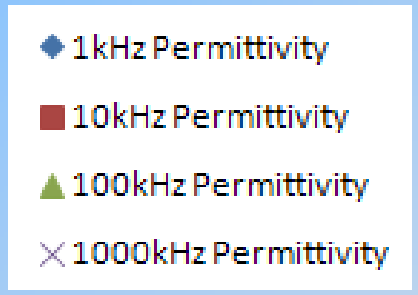
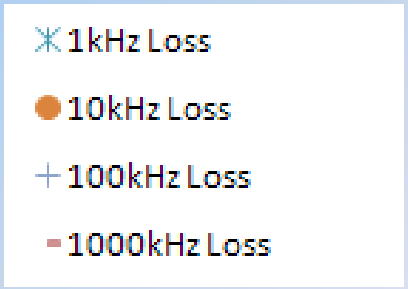
$BaTiO_3$ Nanocomposite Weak-Field Analysis









- **Some change in dielectric loss with the addition of glass**

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Barium Borosilicate Glass

Components	Mole %	Weight %
BaO	50	68.73
SiO_2	20.97	11.29
Al_2O_3	102	0.93
H_3BO_3	24	14.97
ZrO_2	2.01	2.22
SrO	2	1.86

- **Glass sintering aid for BTO/glass nanocomposite**
- **Provided by Missouri University of Science and Technology**

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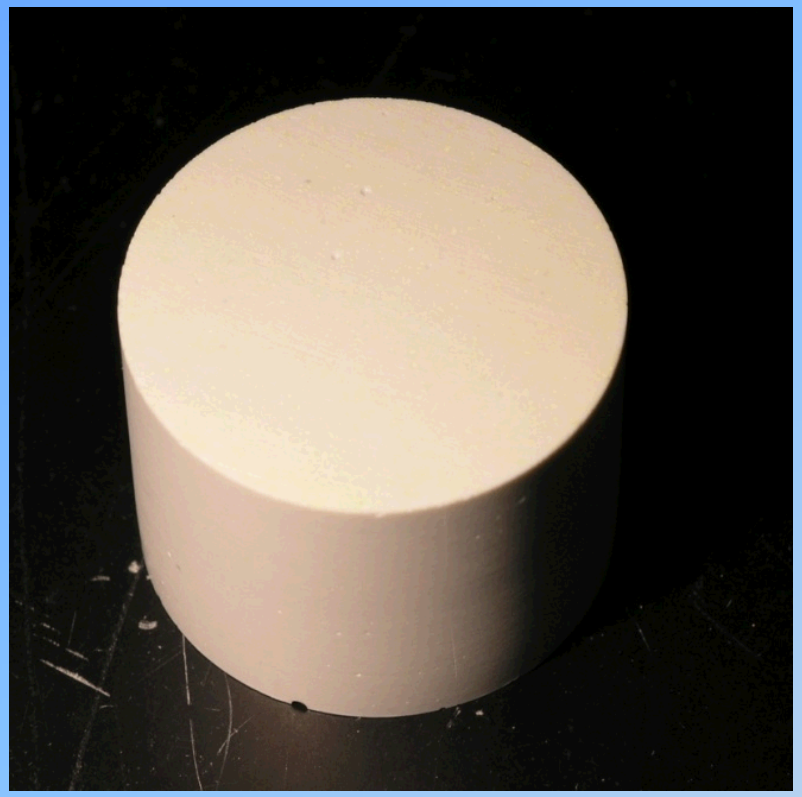
$BaTiO_3$ Nanocomposite High Field Hysteresis



BTO/epoxy nanocomposite

- Epoxy composites will allow rapid testing of different BTO particle syntheses and sizes & optimize system
- Master Bond EP30HT and TPL BTO, 50 w/w %
- We will form composites with BTO nanoparticles that we synthesize next
- Cures with low porosity
- Beginning to dice and coat with electrodes for electrical testing

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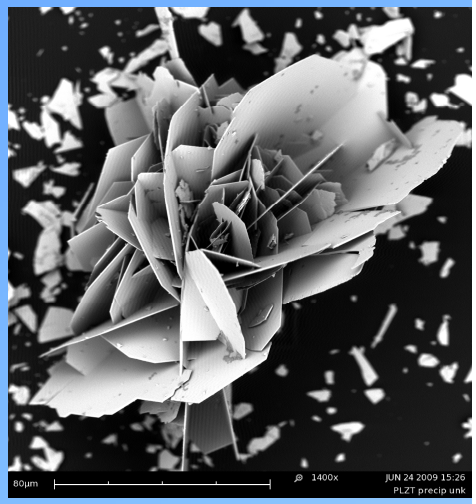
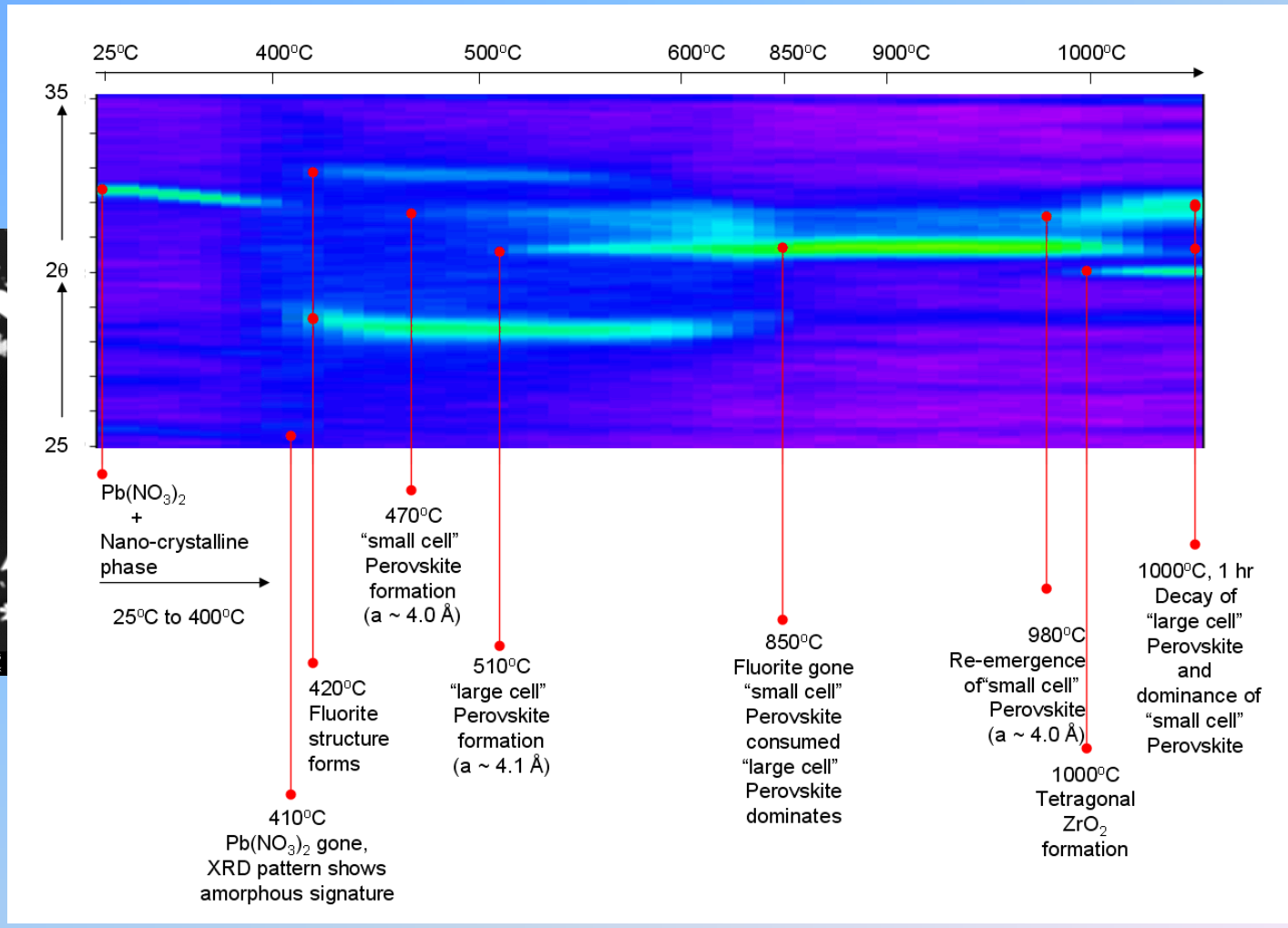
PLZT Results

Previous synthesis: variety of phase evolution paths and several intermediate compositions





Full understanding of raw materials and better chemistry control allows simplification of the synthesis route

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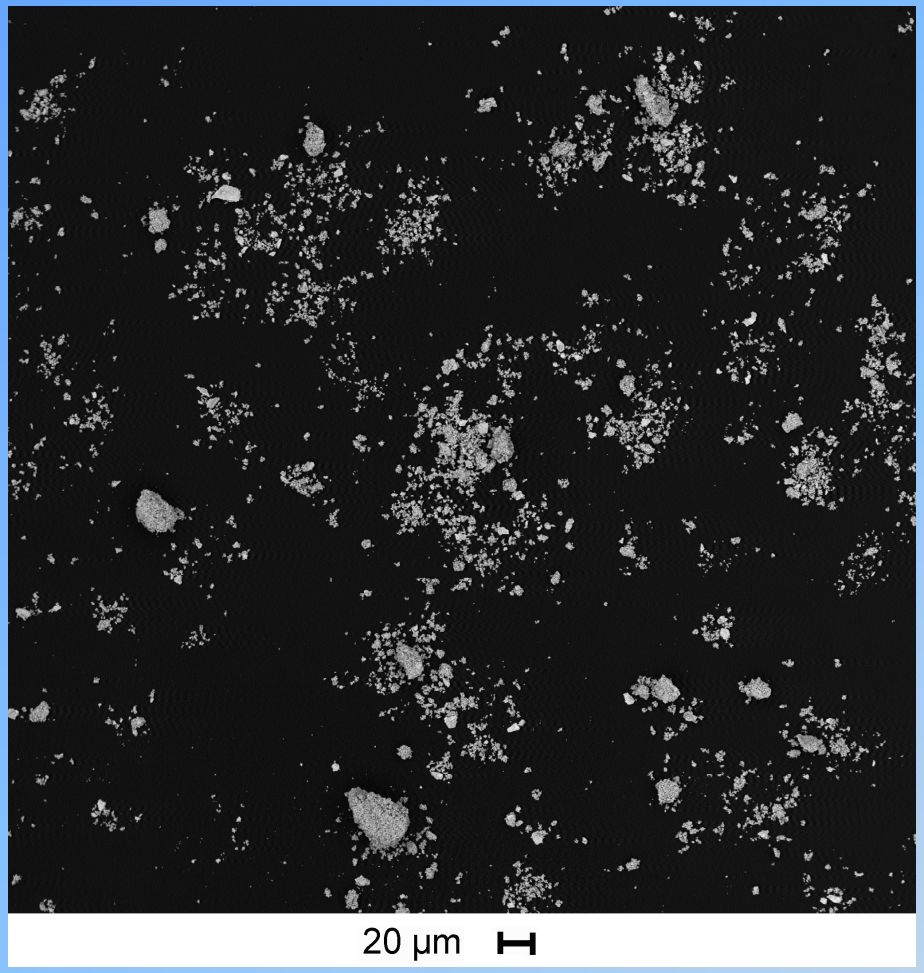
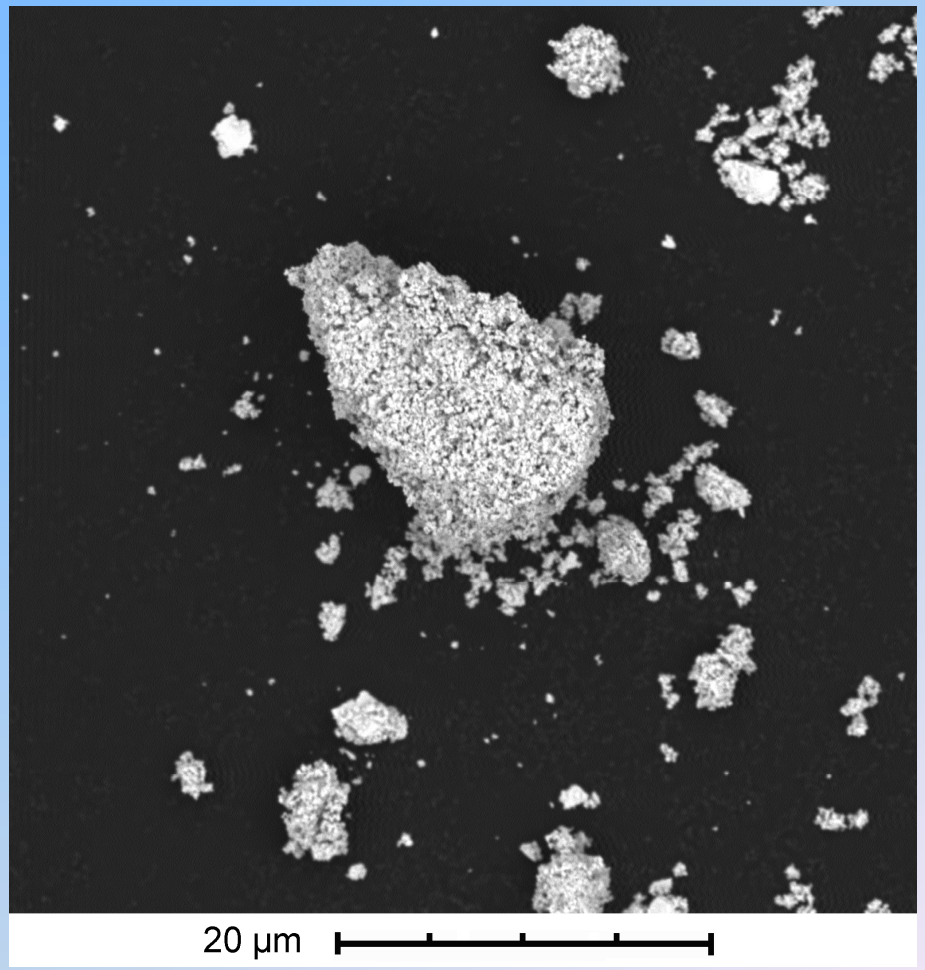
Large calcined particle size, nanoscale crystallite size





While this result was not anticipated, it may facilitate sample fabrication by easing safety issues

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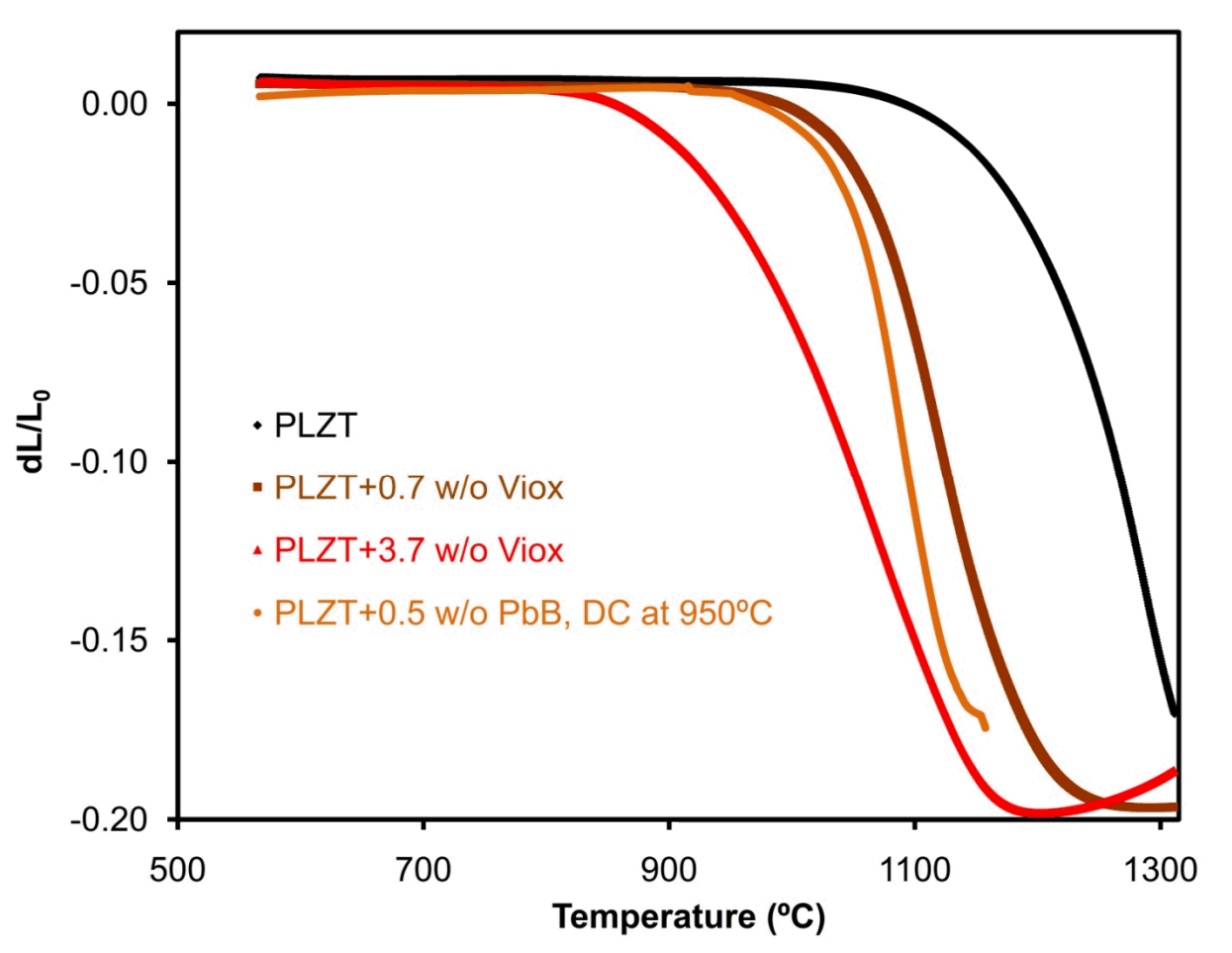
Choice of Glass Sintering Aids



- Several glass sintering aids are available
- Optimizing the chemistry and quantity is essential

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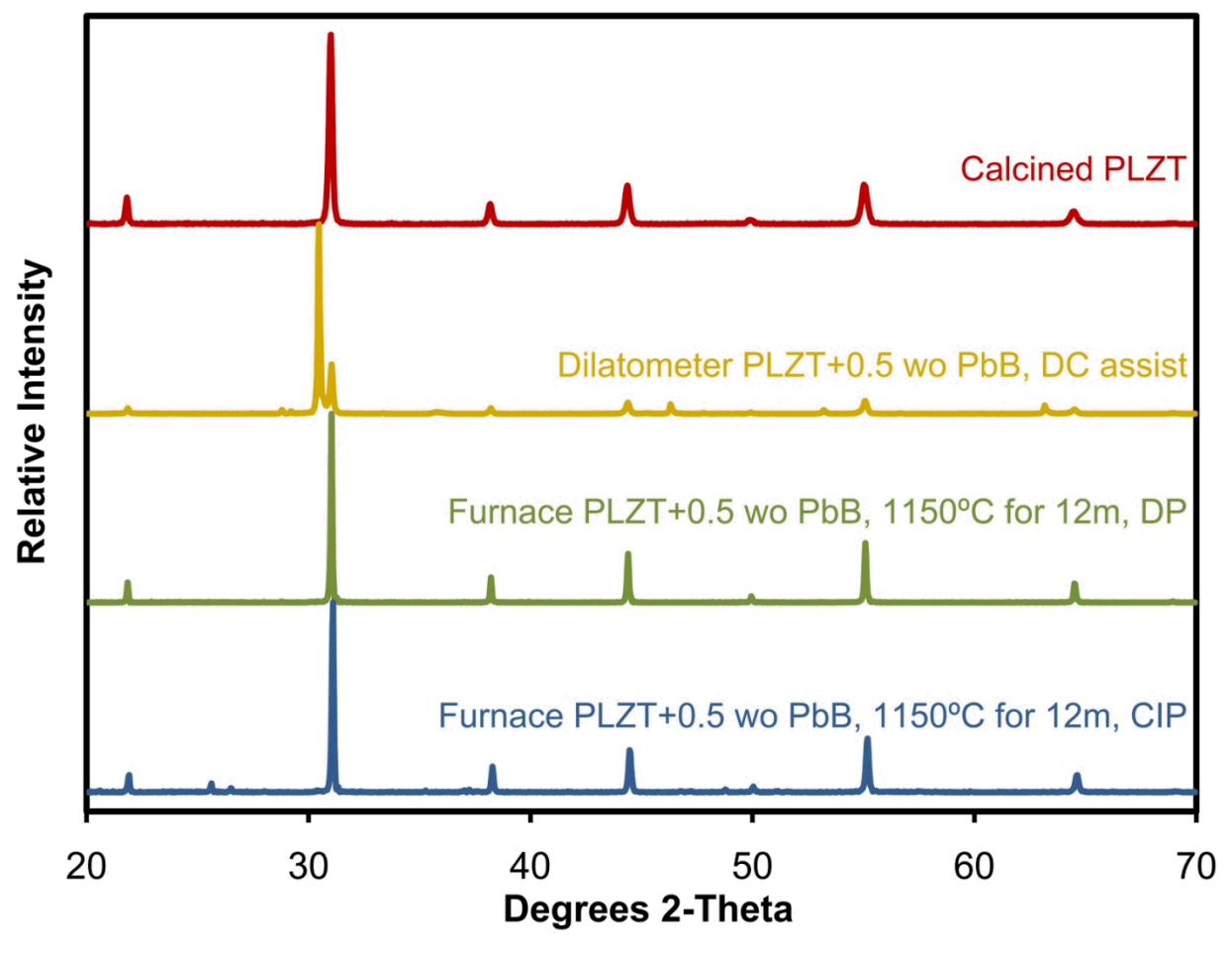
Post-Sintering XRD



- **Secondary surface phases are present after dilatometer sintering**
  - **Likely due to platinum reaction or uncontrolled atmosphere**

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