Development of Low-Cost, Compact, Reliable, High Energy Density Ceramic Nanocomposite Capacitors

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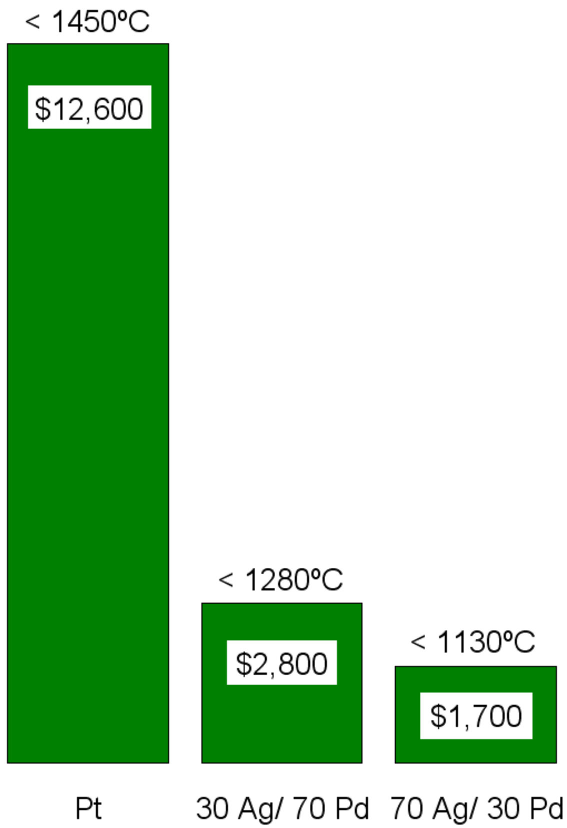
Ceramic Nanocomposite Capacitor Goals



- **More than double energy density of ceramic capacitors (cutting size and weight by more than half)**
- **Potential cost reduction (factor of >4) due to decreased sintering temperature (allowing the use of lower cost electrode materials such as 70/30 Ag/Pd)**
- **Lower sintering temperature will allow co-firing with other electrical components**

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Benefits of Nanocrystalline Dielectrics

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

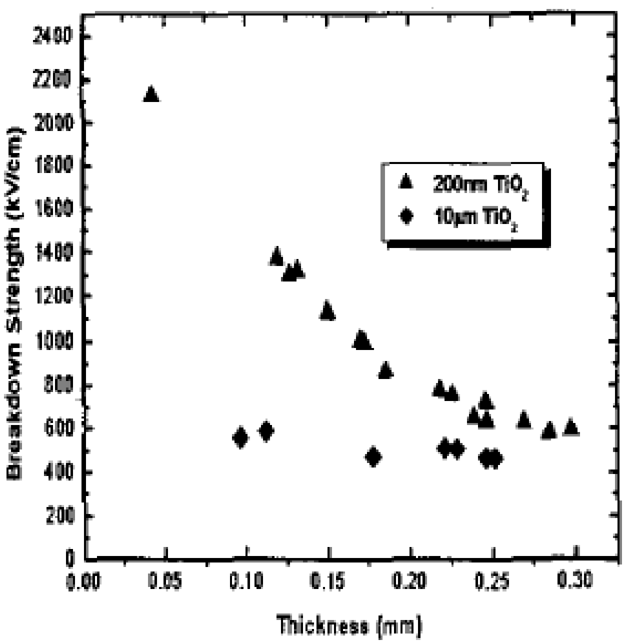

Figure 5. BDS as a function of dielectric thickness for nanocrystalline- and coarse-grained TiO_2.

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

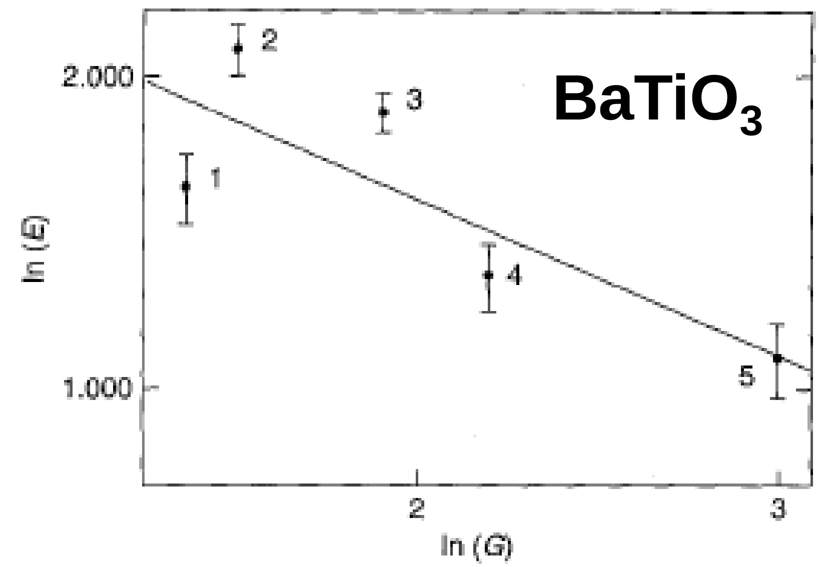

Figure 2 Grain size dependence on dielectric strength. Numbers indicate sintering temperatures: (1) 1320 °C, (2) 1330 °C, (3) 1350 °C, (4) 1380 °C, (5) 1400 °C.

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)**

Ying and Hsieh, *Mater. Sci. Eng., B* **138** 241 (2007)

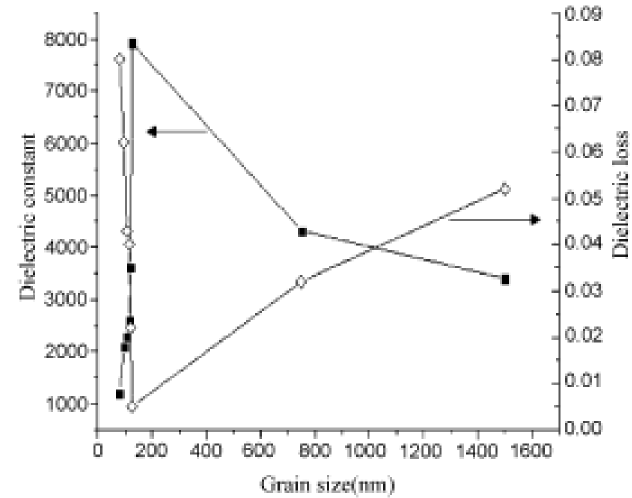


Fig. 7. 1 kHz dielectric constant and dielectric loss vs. grain sizes of nano-$BaTiO_3$ sintered at 1100 °C.

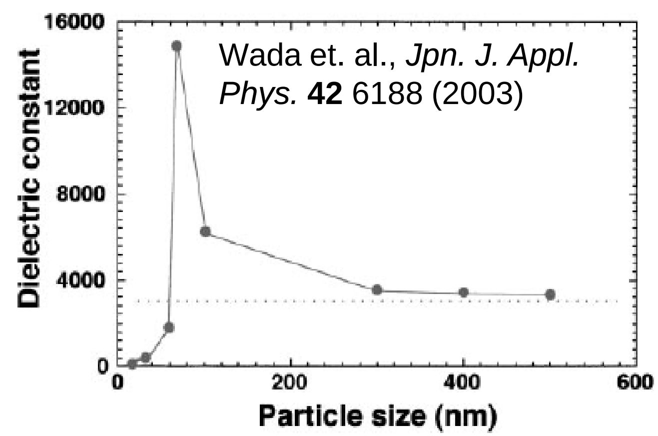


Fig. 15. Particle size dependence of the dielectric constants of the $BaTiO_3$ powders.

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**

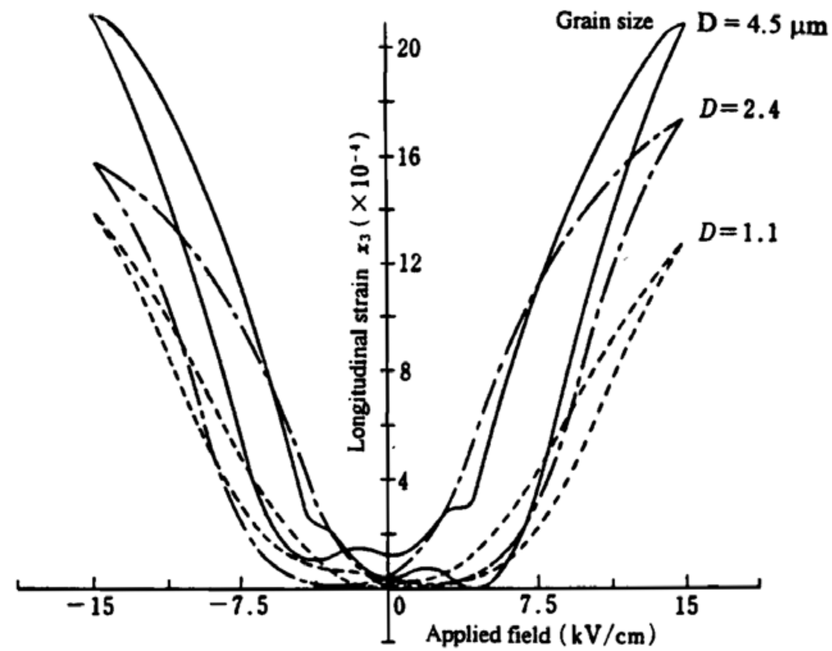
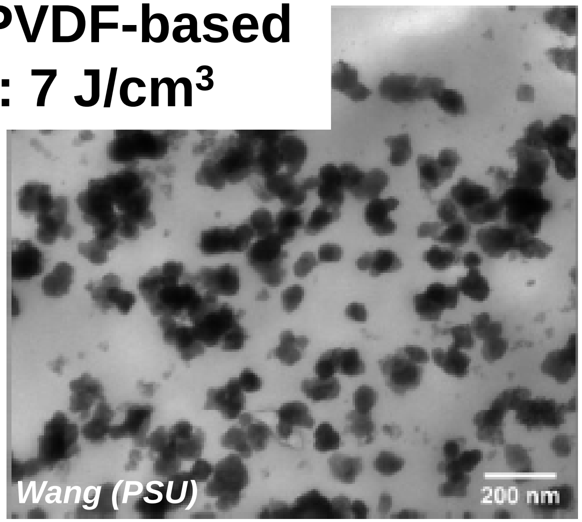


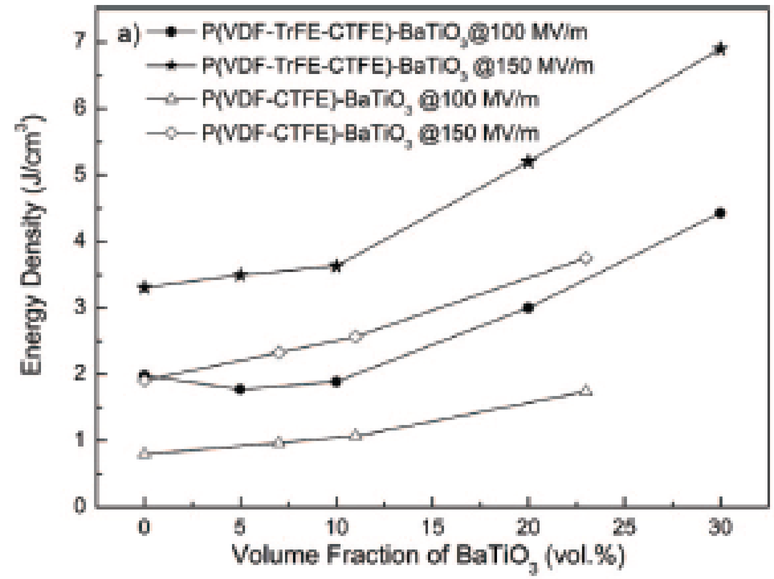
Fig. 3.28 Grain size dependence of the induced strain in PLZT ceramics.

from Kenji Uchino's book, Ferroelectric Devices

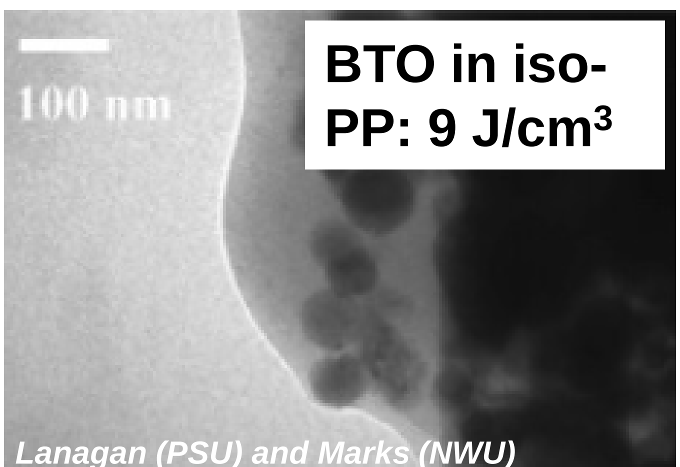
Polymer-Based Nanocomposite Dielectric Films

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





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



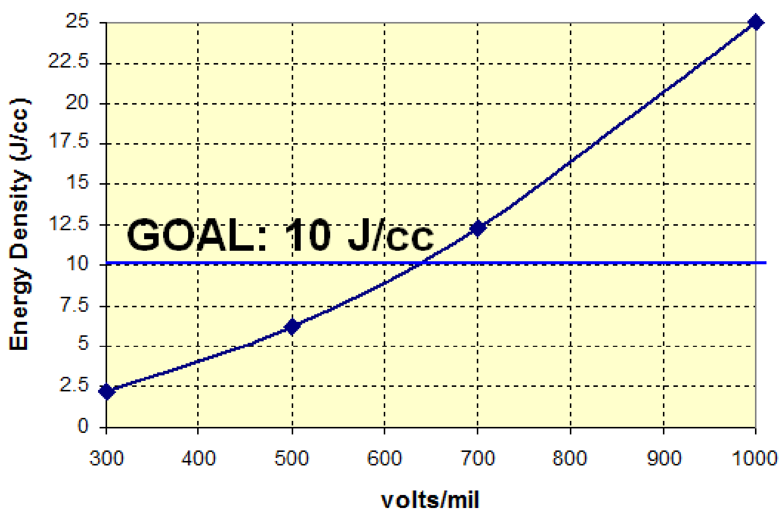
- **High energy densities demonstrated, but proof of performance in devices is lacking**
- **Low volumetric fraction of the inorganic particles (~ 25-30% loading)**
- **Size effects in ferroics not exploited**

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



Assumptions:
10% glass by volume, ε_r=3
90% $BaTiO_3$ by volume, ε_r=8000
➔ ε_{eff} = 3635

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Additional Benefits of Ceramic/Glass Nanocomposite Solution

- **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 in excess of 500 V/mil**
- **More robust devices**

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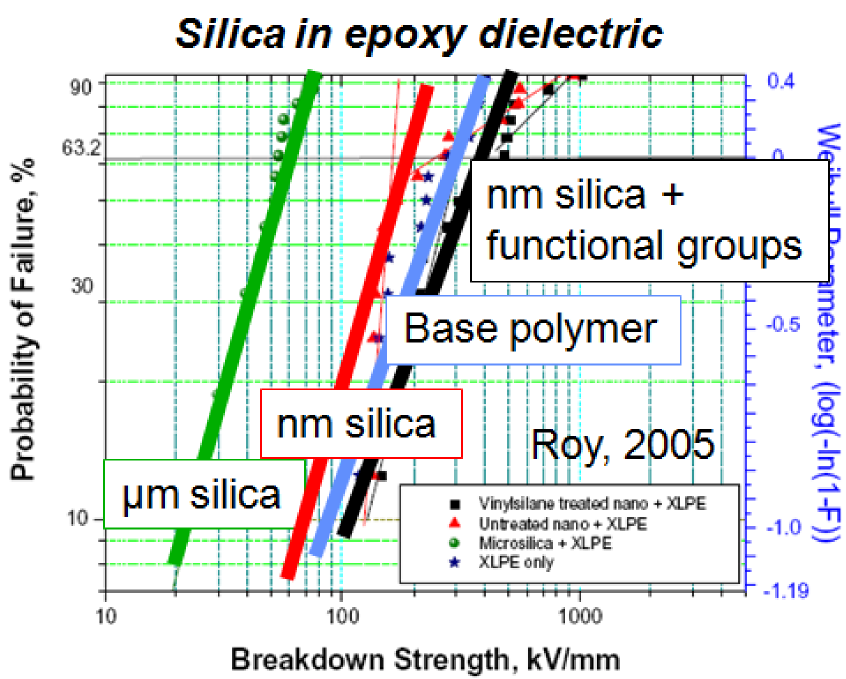
Integration into Multilayer Configuration

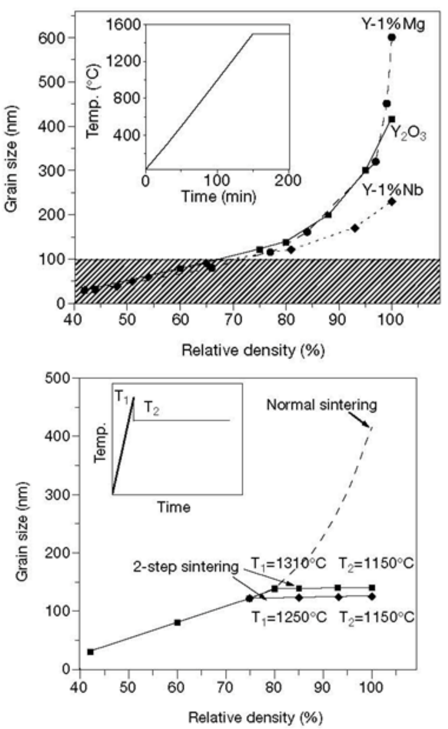
Lab-scale tape casting setup

- 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

Ceramic Nanocomposite Capacitor Challenges

- Challenges
  - Nanocrystalline material synthesis, particle size and distribution
  - Processing and forming
    - Agglomeration/dispersion, minimizing porosity, high material density
  - Suitable and compatible matrix material, maintain desired crystal structure/phase
  - Prevent activation of excessive grain growth, maintain nano-sized grains





Chen, Nature, Vol 404, March 9, 2000

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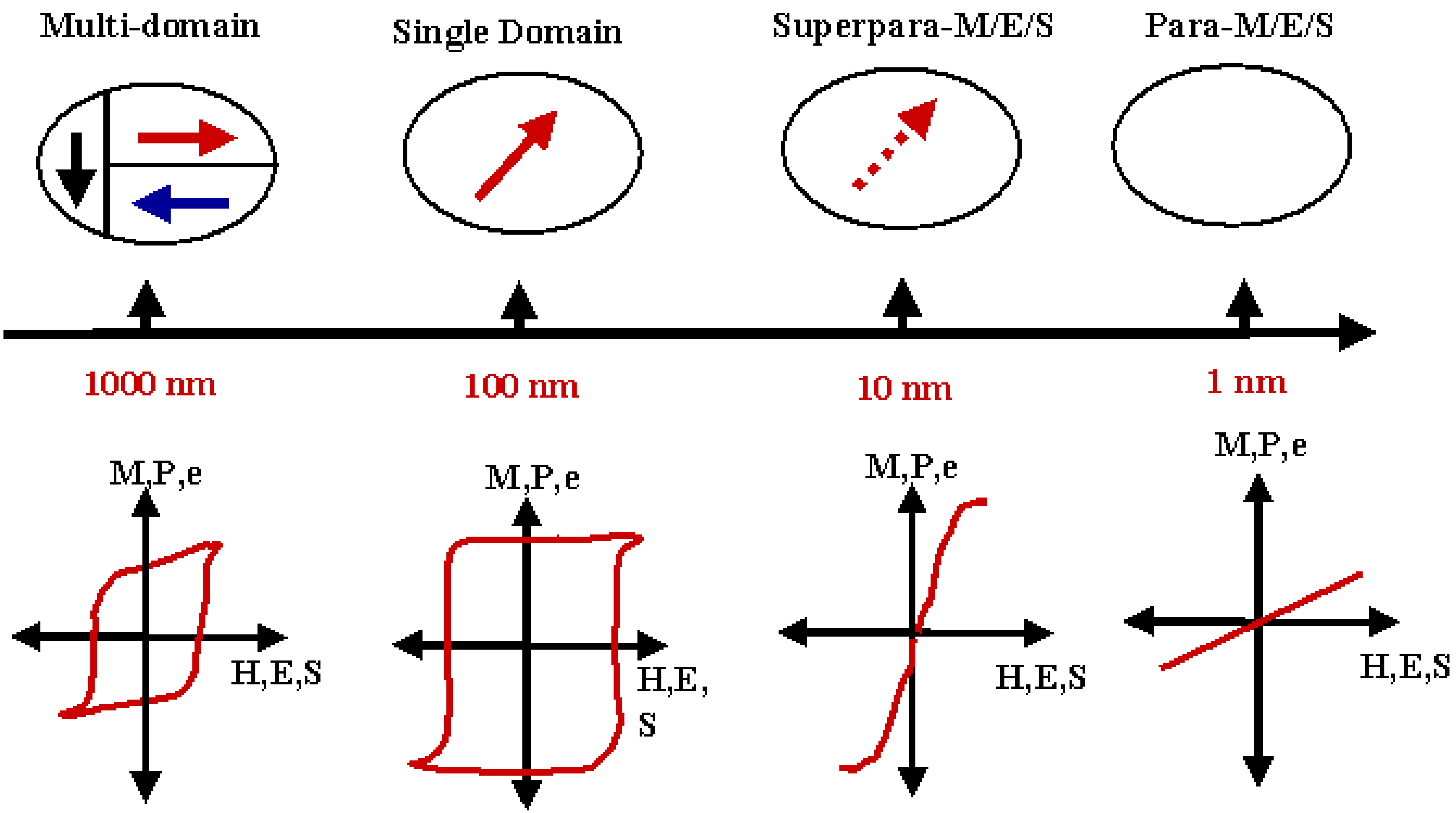
SIZE EFFECTS IN FERROICS (R. E. Newnham, 1992)

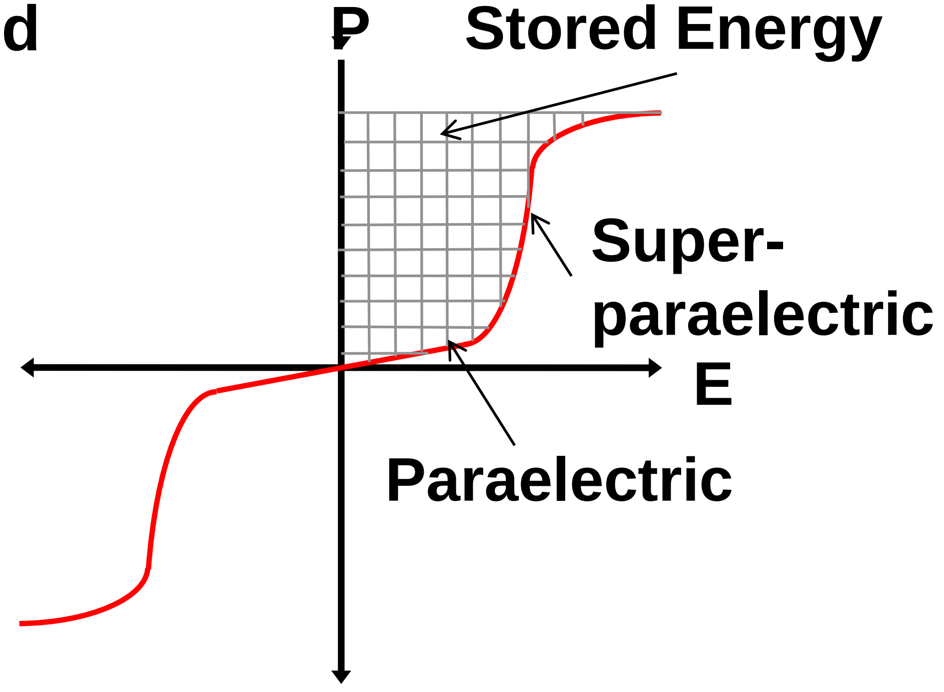


Transitions expected in *Ferromagnetics*, *Ferroelectrics* and *Ferroelastics* as a function of size.....

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

Increased Energy Density Through Phase Transformation

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



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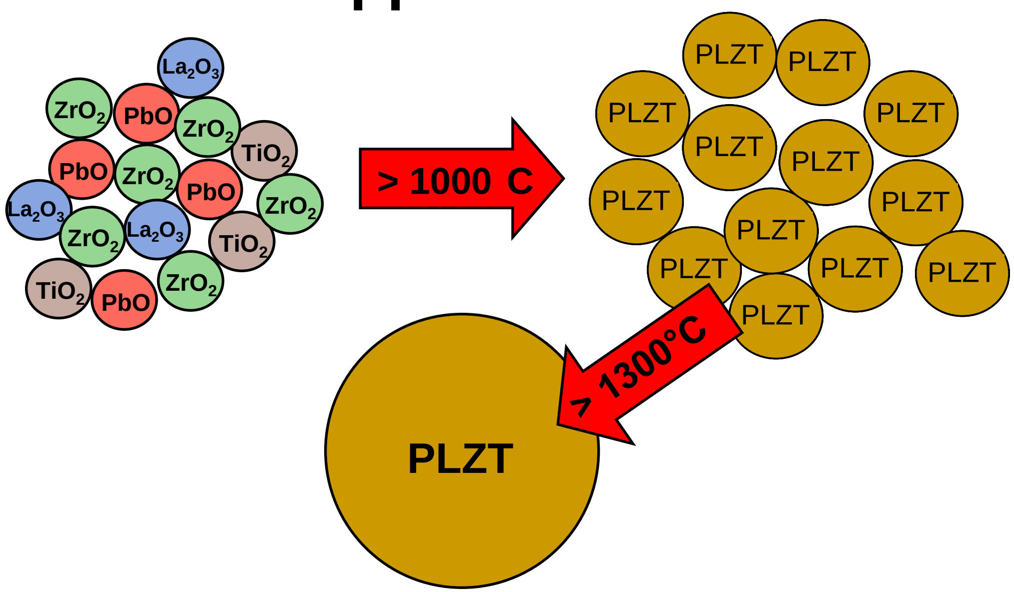
Materials Approach

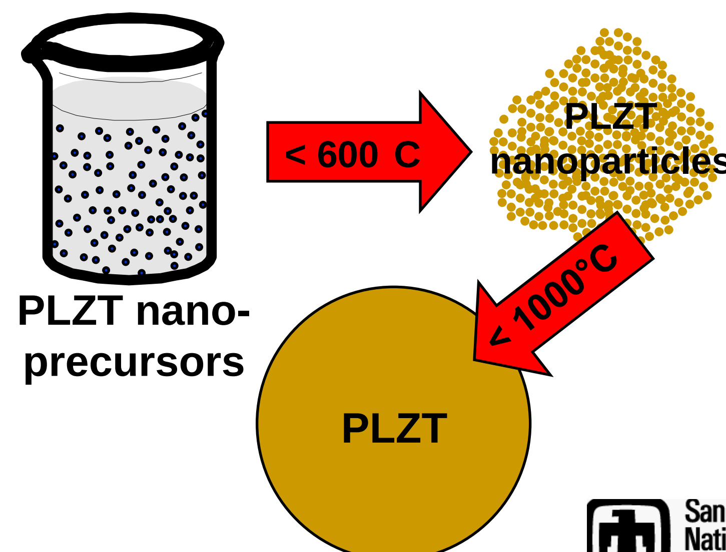
Approach:

- **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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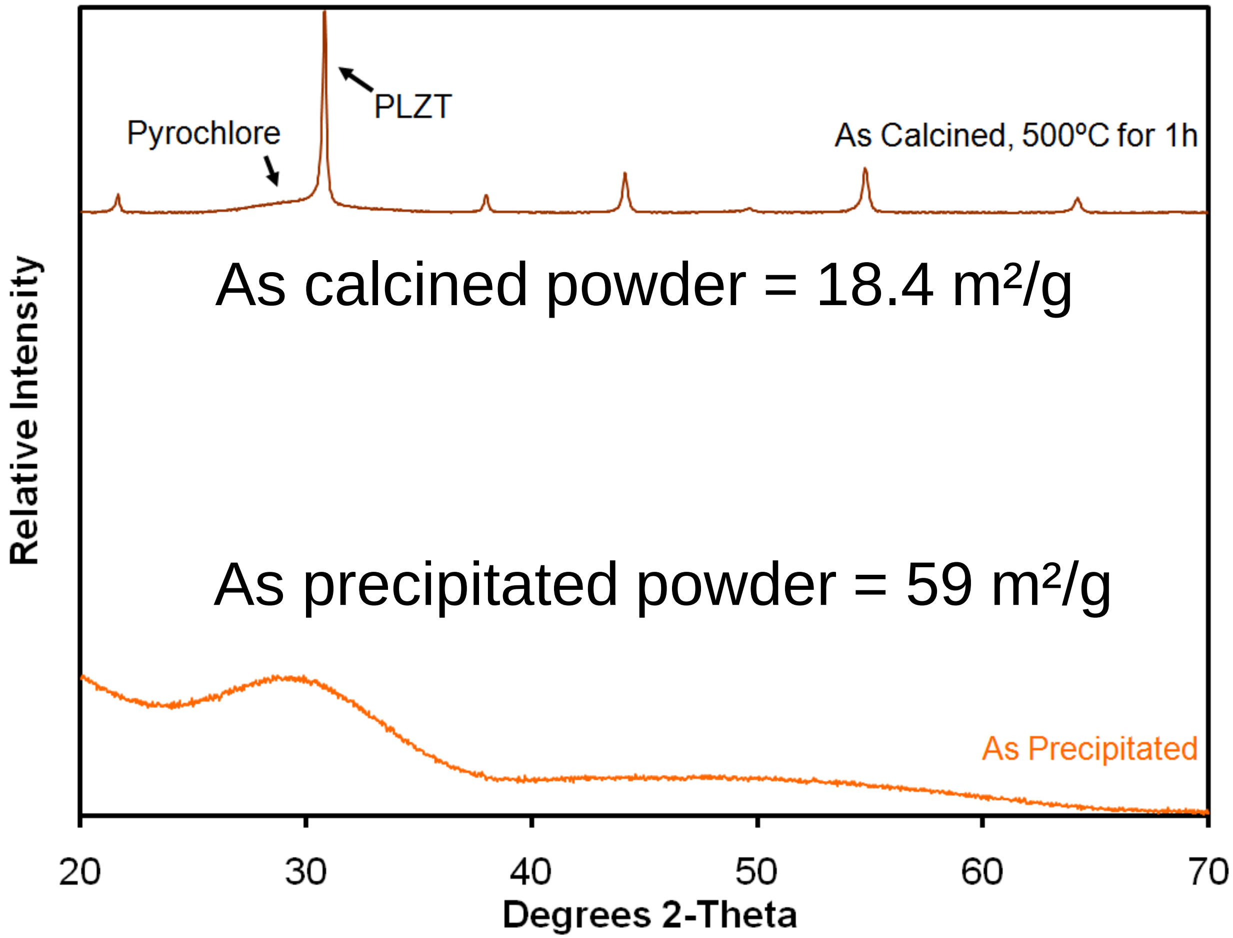
PLZT Nanoscale Precursor Synthesis and Calcination



Scherrer equation analysis of XRD data gives a crystallite size of 38.5 nm

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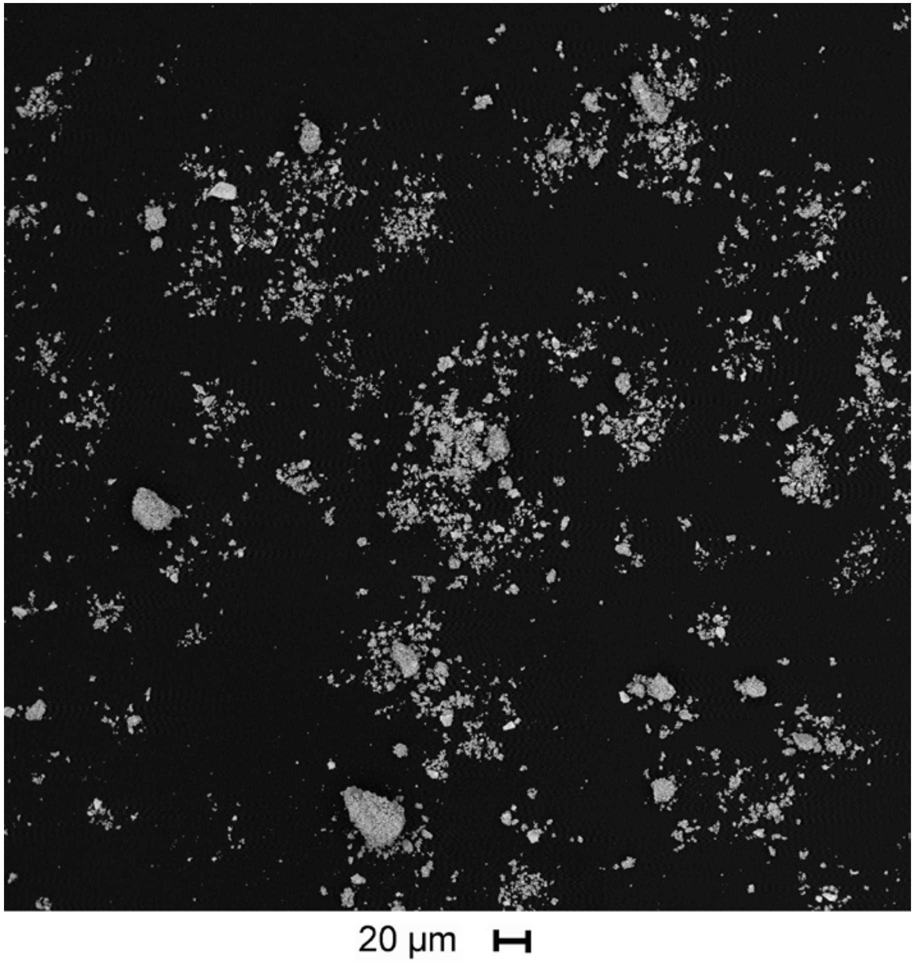
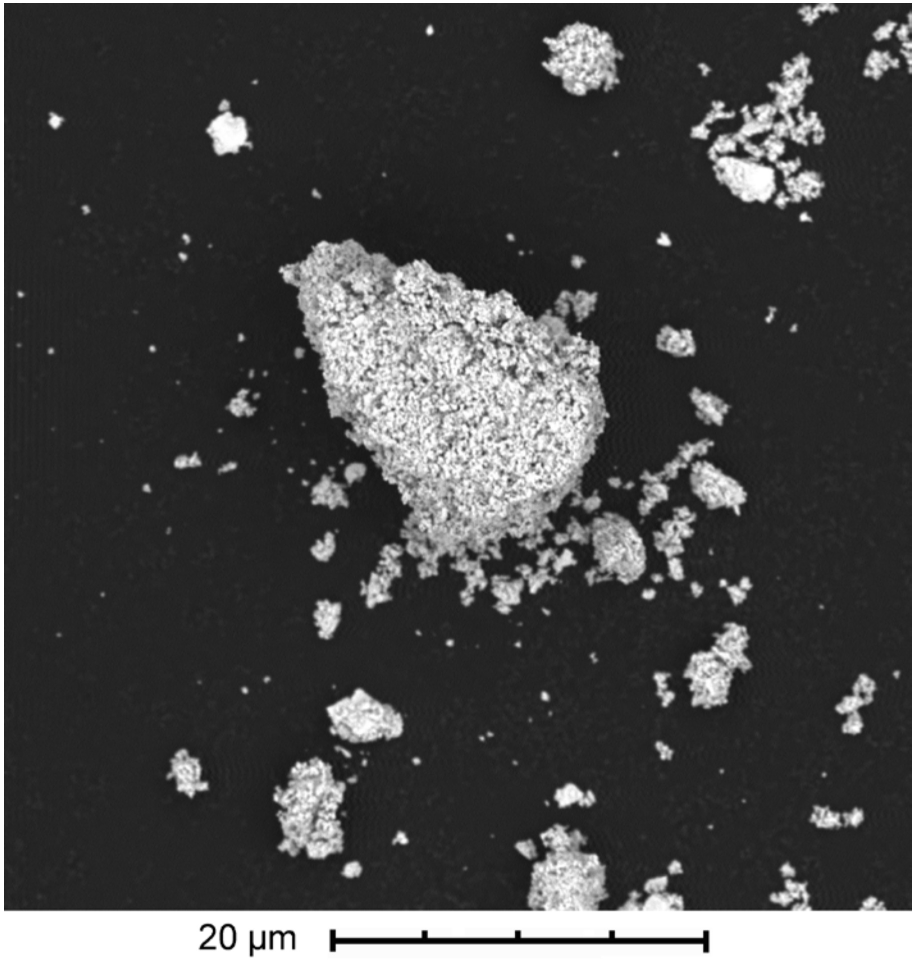
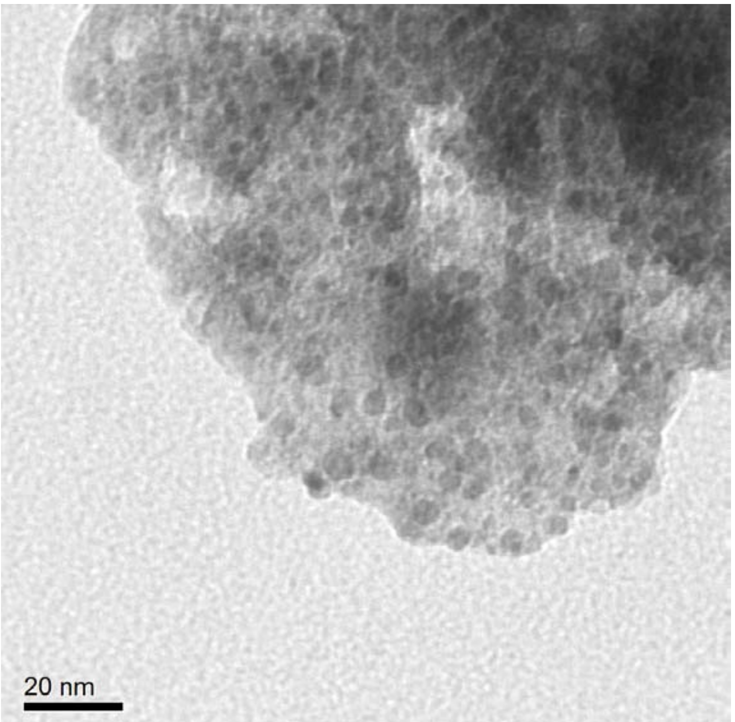
Large calcined particle size, nanoscale crystallite size

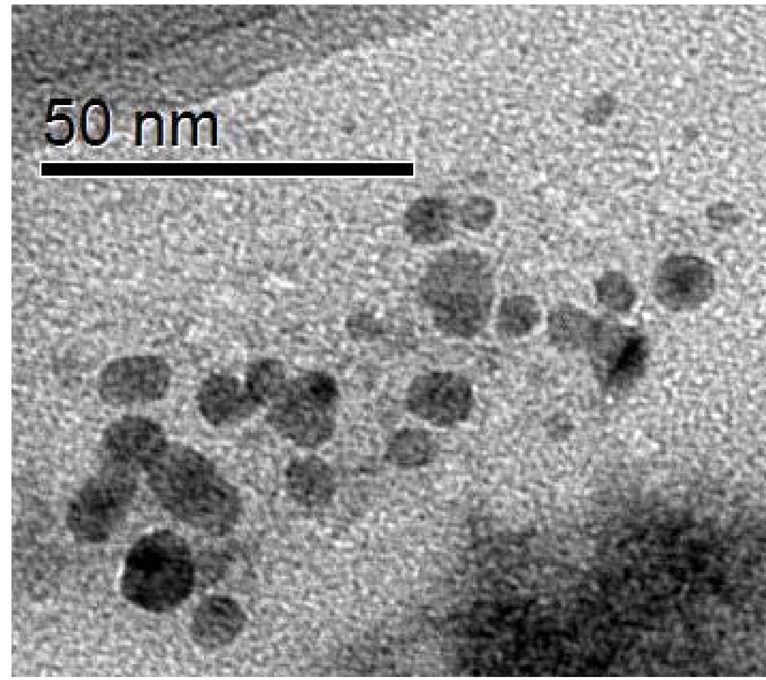




While this result was not anticipated, it may facilitate sample fabrication by easing safety issues

TEM of nanocrystalline grains





TEM imaging reveals nanocrystalline grains in calcined PLZT

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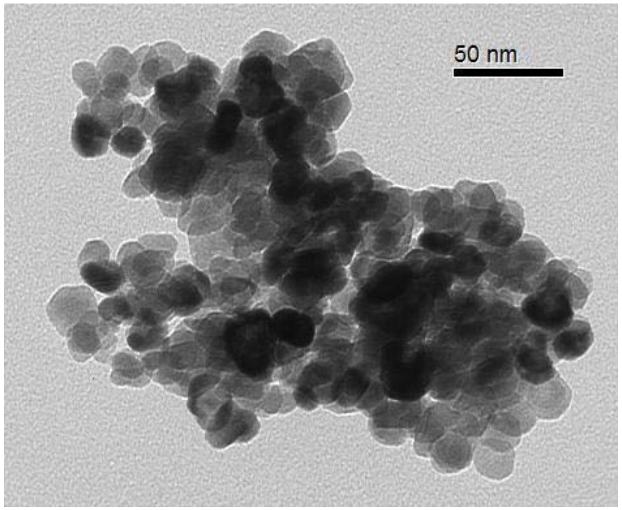
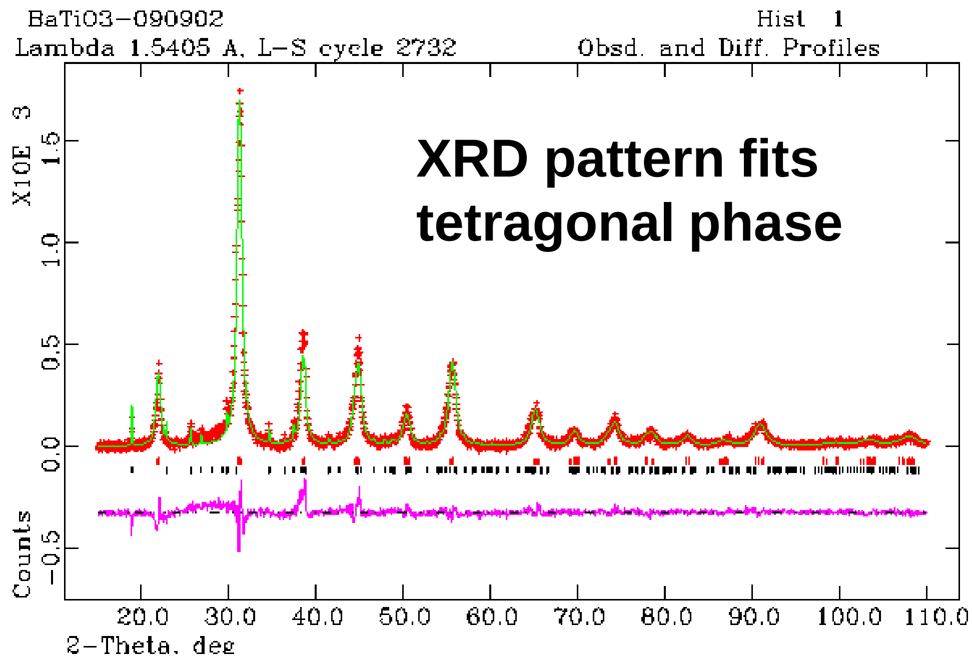
$BaTiO_3$ Nanoparticle Synthesis, $Ba(OH)_2 \cdot 8H_2O$ Reagent

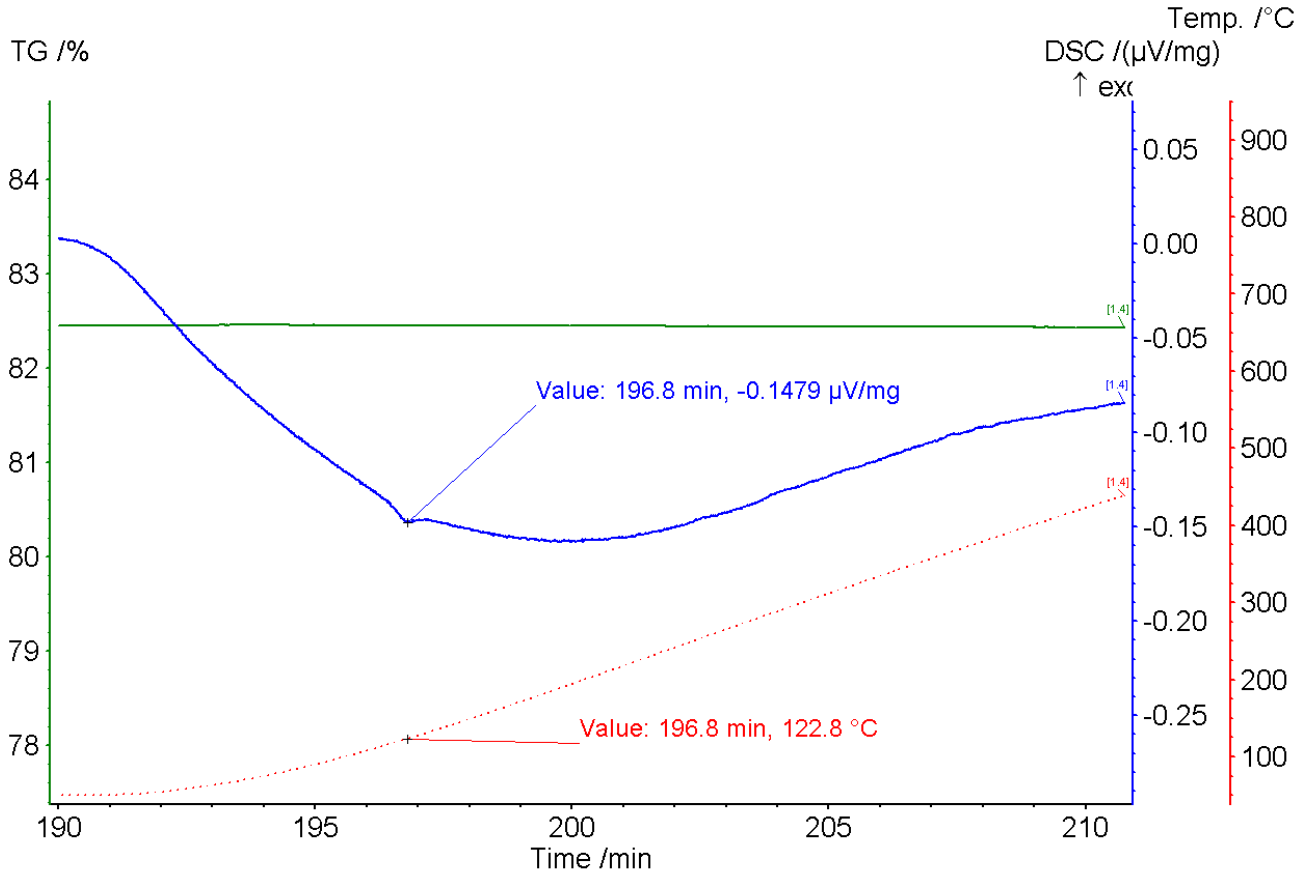




- $Ba(OH)_2 \cdot 8H_2O$ and $Ti(OPr)_4$ precursors
- Redesigned synthesis using air-free chemistry and with improved control over water addition
- Modified synthesis for our dry environment through extra H_2O addition
- XRD indicates tetragonal phase present when particles synthesized with 0.5 and 0.6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

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

$BaTiO_3$ 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)**

Conclusions & Future Work

- Benefits of Glass/Ceramic Nanocomposite Clear
- Facilitating first commercialized glass/ceramic nanocomposite
- Room temperature, aqueous, scalable syntheses for both PLZT & BTO developed

Future Work:

- Device fabrication and electrical testing
- Co-precipitate grain growth inhibitors and/or sintering aids on nanoparticle surface (i.e., “core/shell” structure)
- Use novel densification approaches (2-step sintering, liquid phase sintering, etc…)

Acknowledgements

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Don Overmyer

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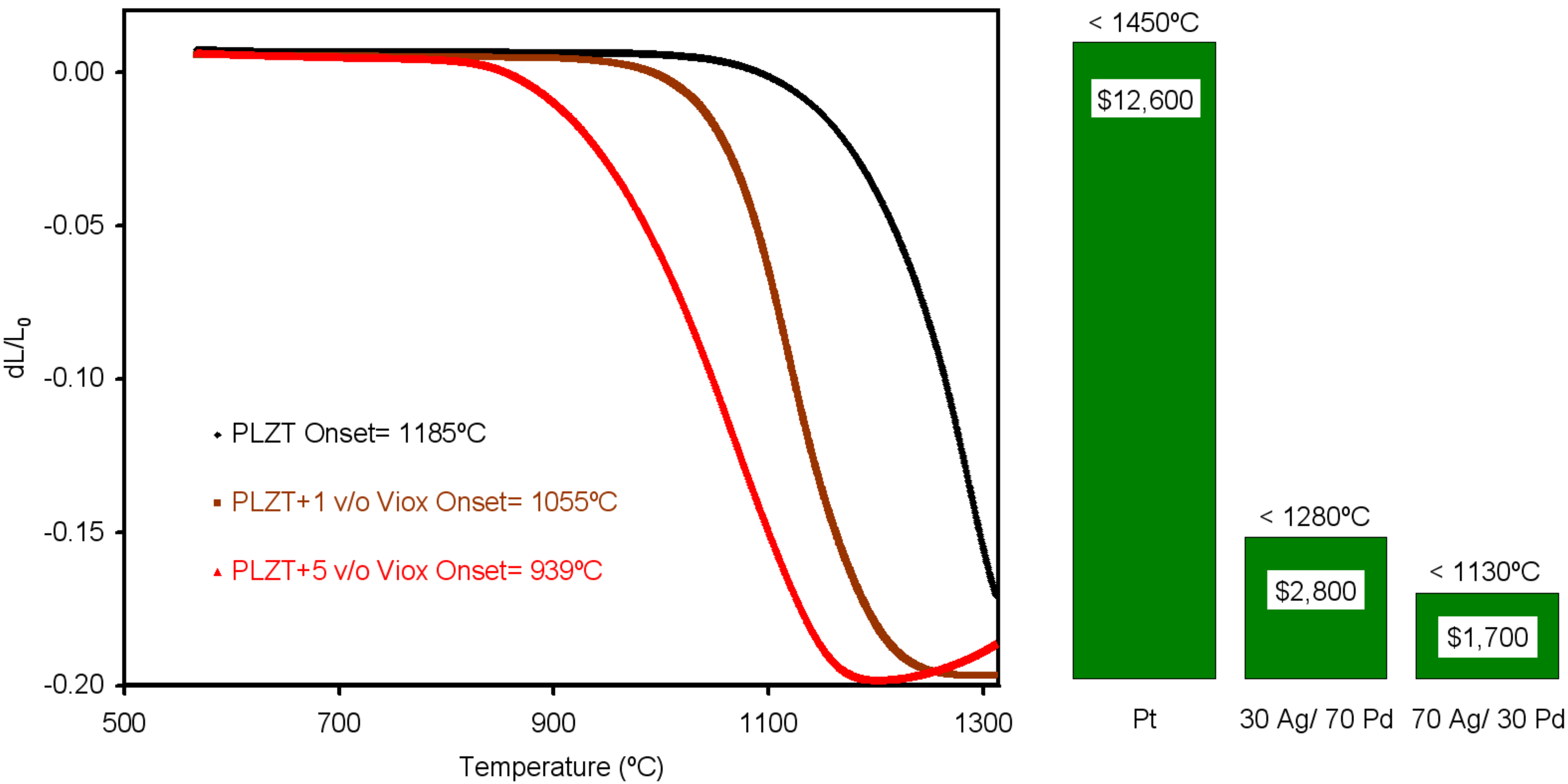
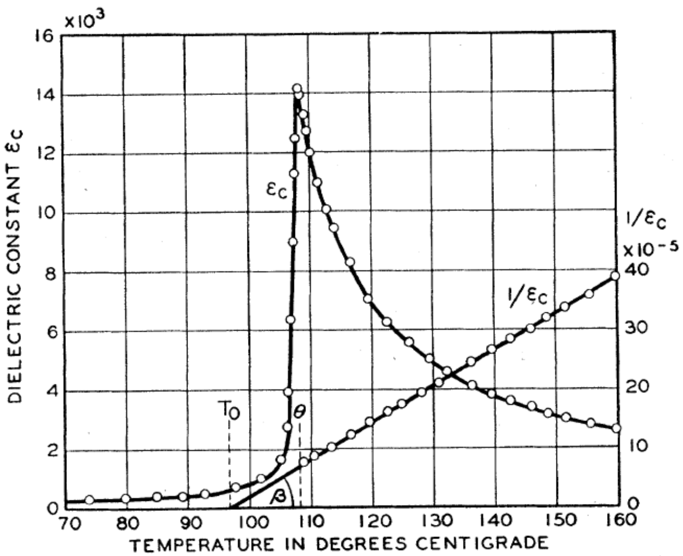
Extra Slides

Glass addition allows the use of a less expensive electrode and reduced lead volatility

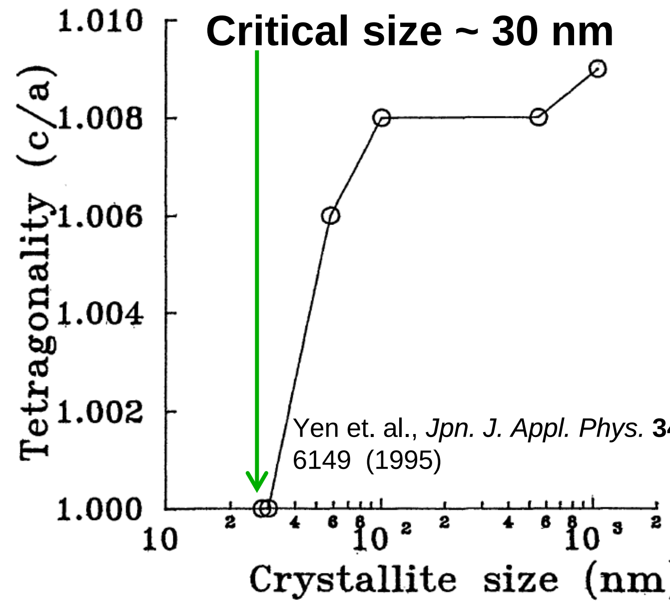


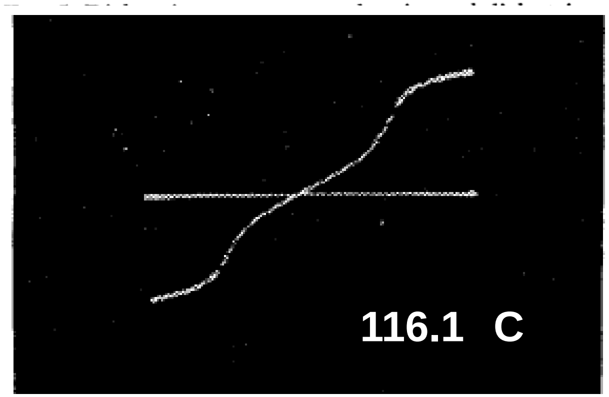
Exploiting Size Effects for High Energy Density Dielectrics

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

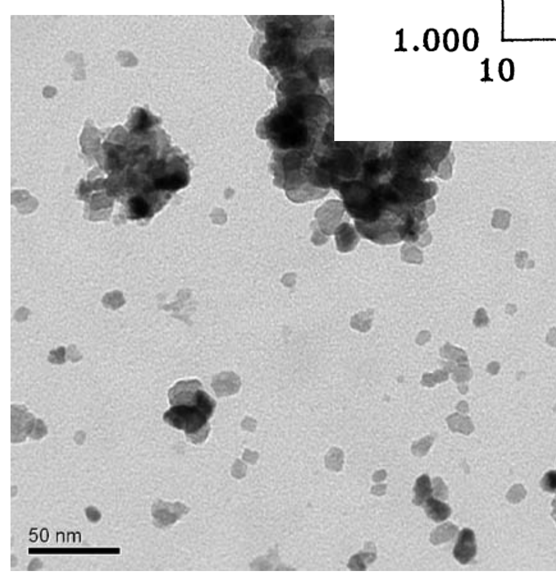


$$KV \approx k_B T$$





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



SNL BTO nanoparticles prepared from chemical synthesis route

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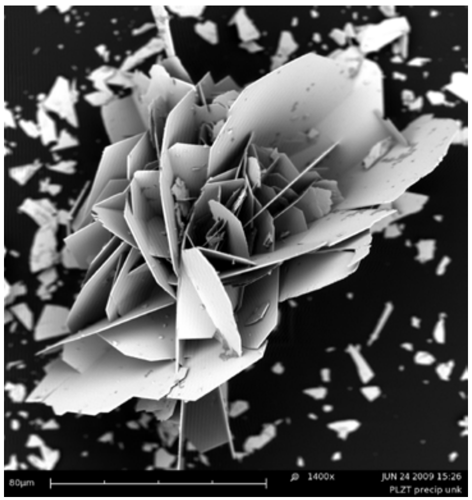
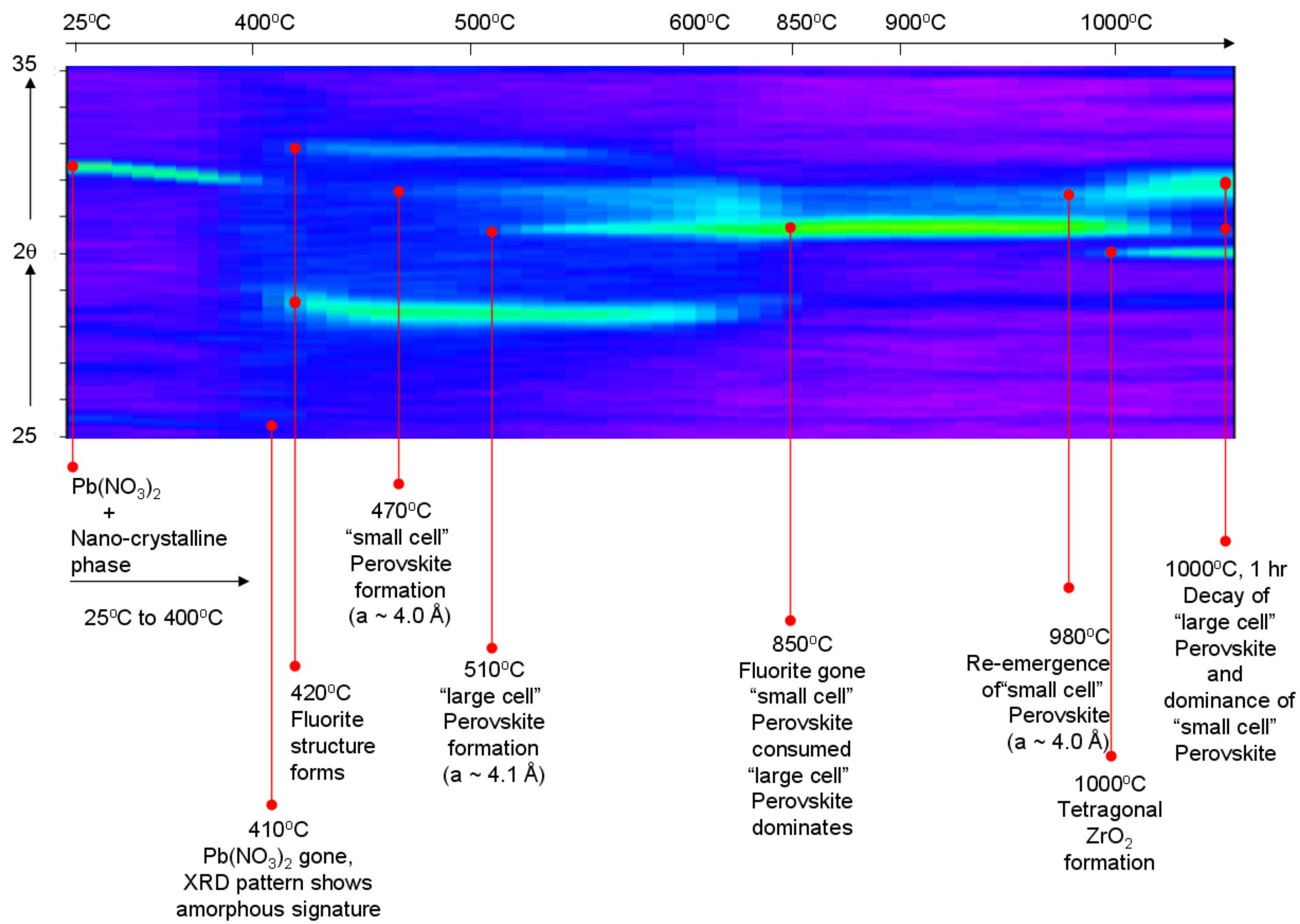
Previous synthesis: variety of phase evolution paths and several intermediate compositions





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

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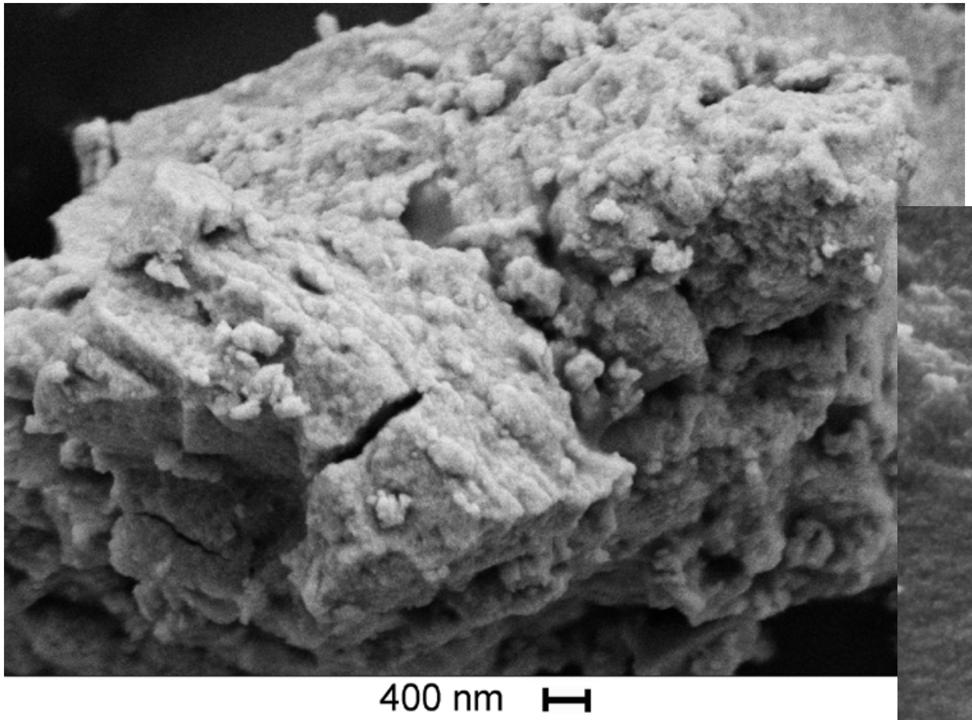
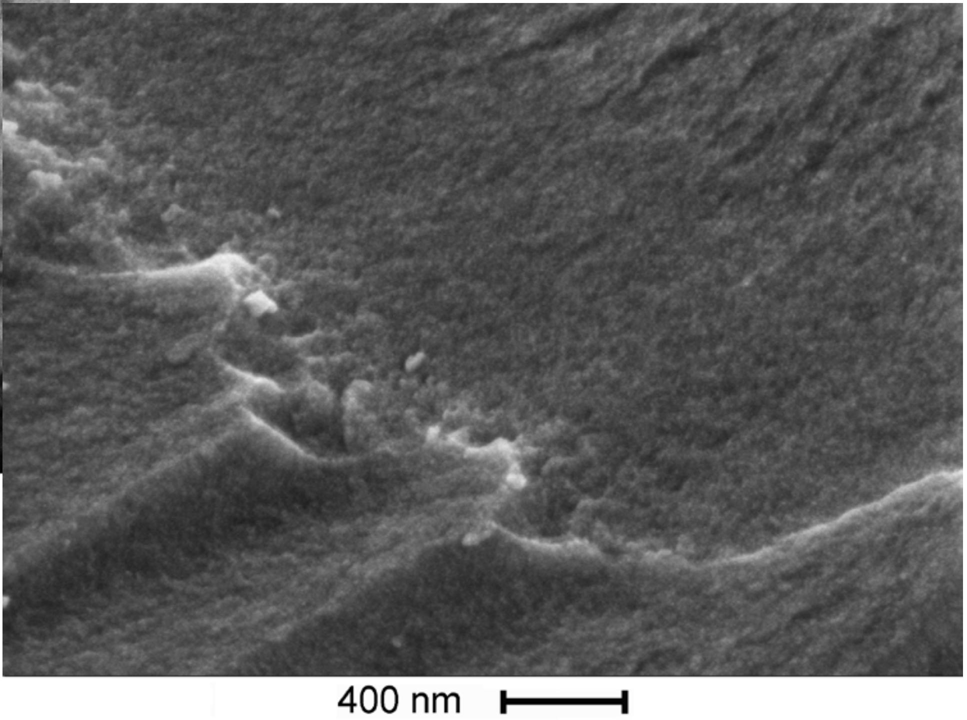
As-dried precipitate shows uniform morphology and no elemental segregation





Atomic homogeneity is key to achieving a phase-pure PLZT at low calcining temperatures

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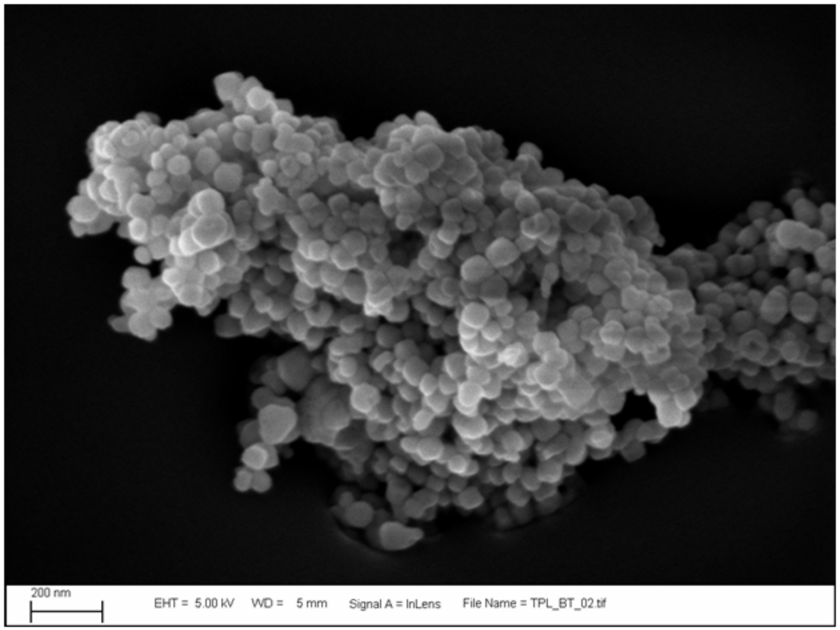
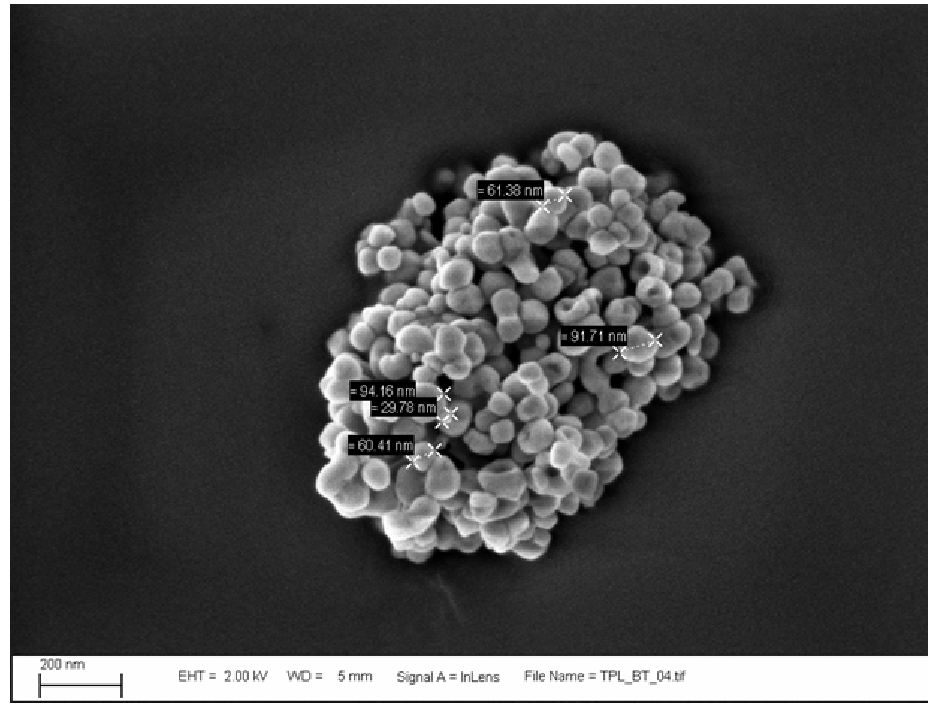
$BaTiO_3$ from TPL





- **NanOxide HPB-1000 from TPL**
- **BET surface area of 16.26±0.0669m^2/g**
- **Attrited to BET surface area of 18.65±0.0459m^2/g**

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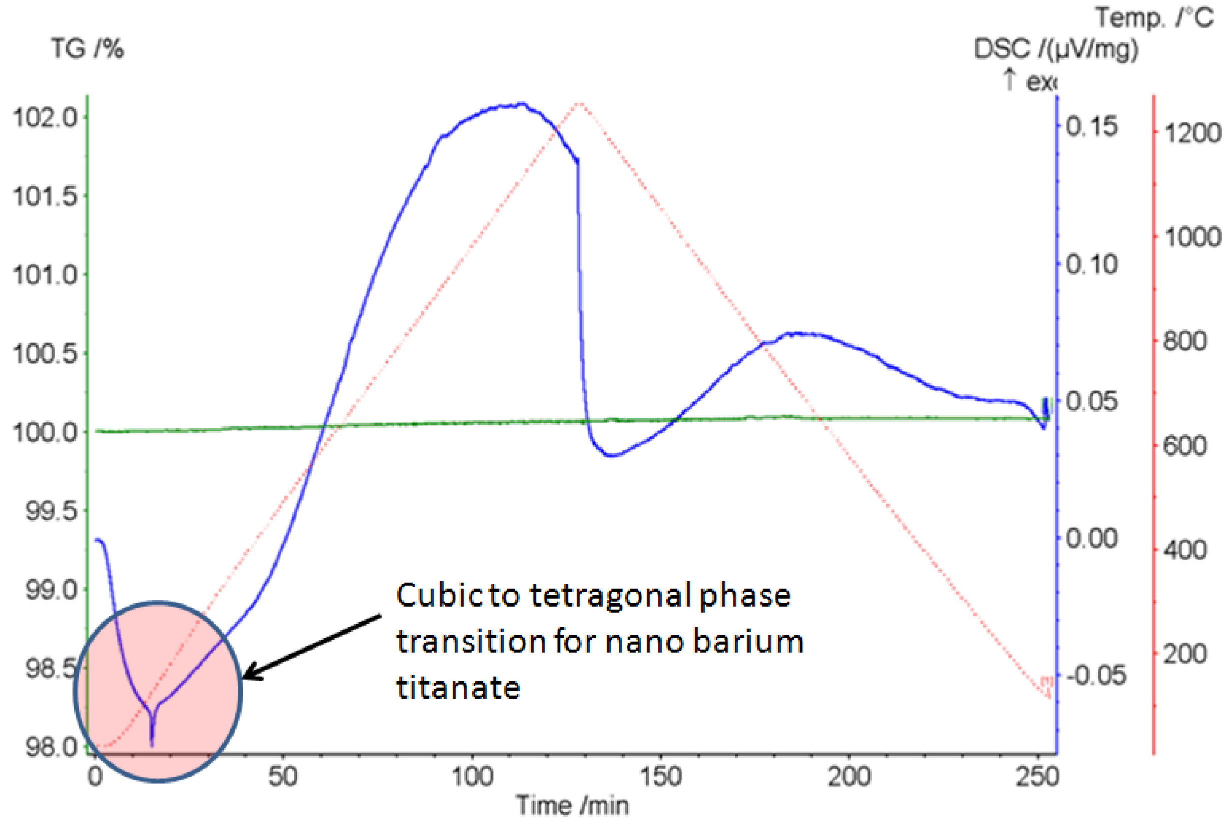
$BaTiO_3$ from TPL



- **Simultaneous thermal analysis (STA)**
- **Cubic to tetragonal 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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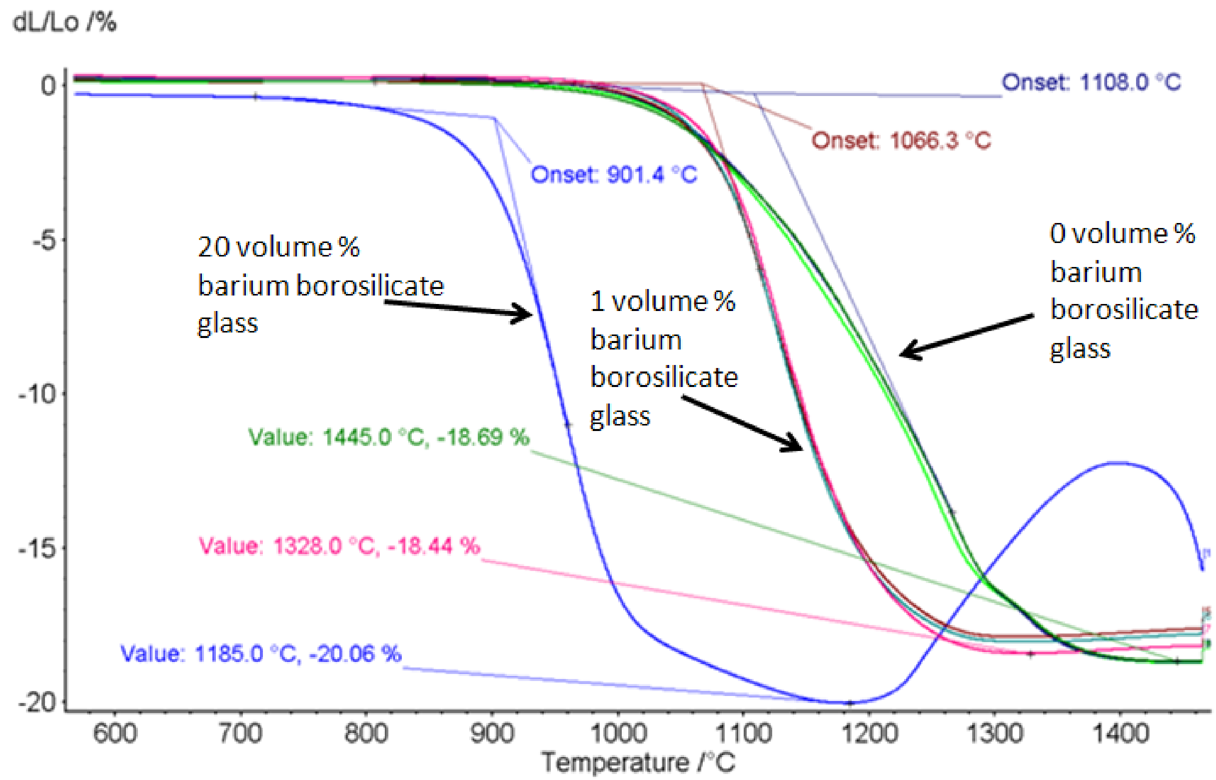
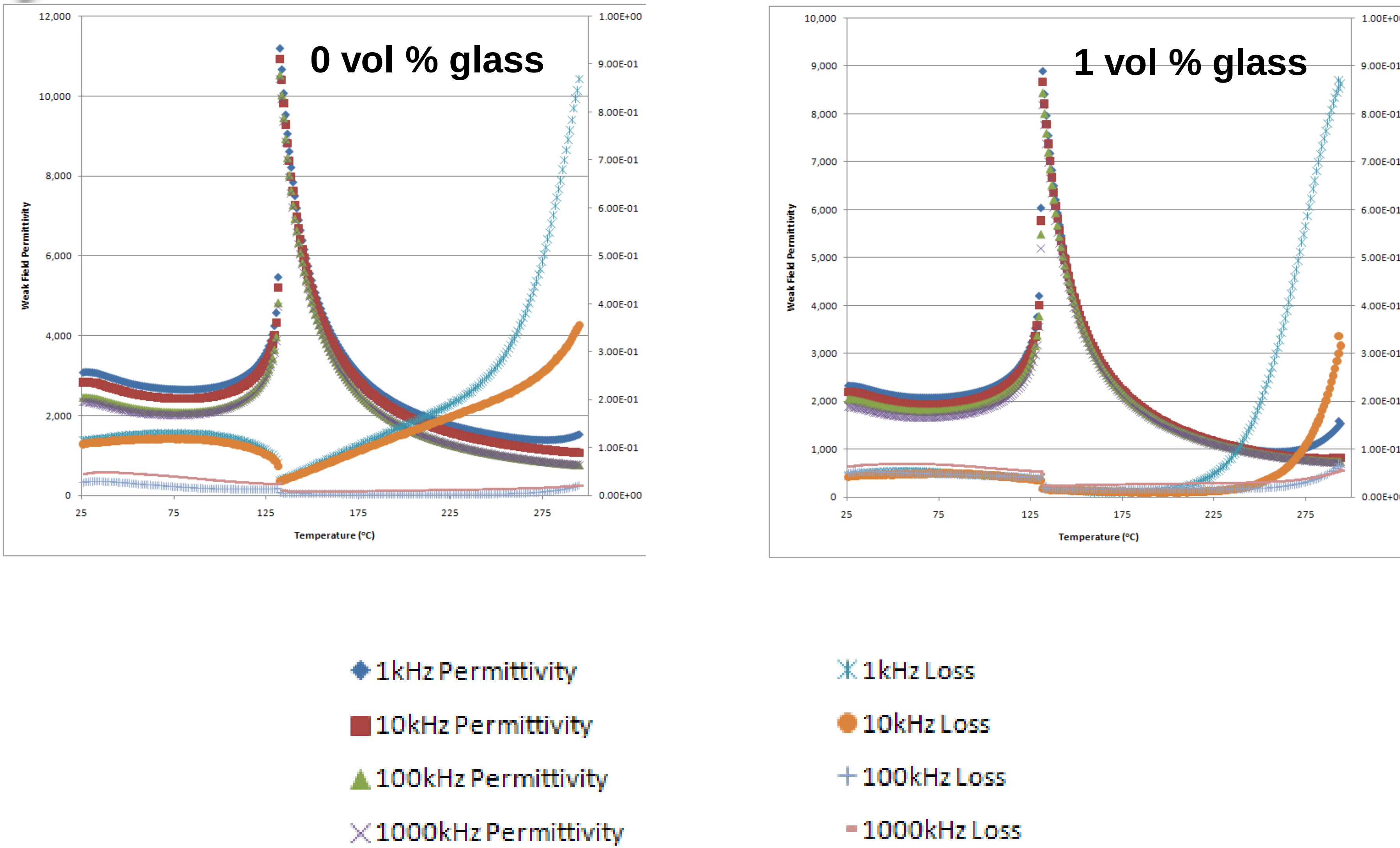
$BaTiO_3$ Nanocomposite Devices

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**

$BaTiO_3$ Nanocomposite Weak-Field Analysis



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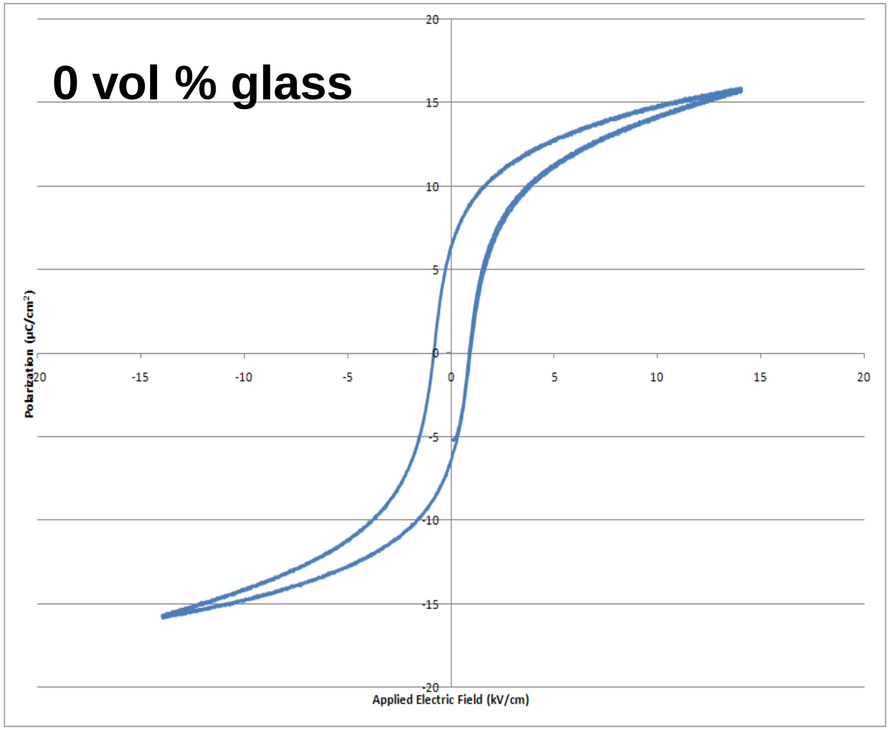
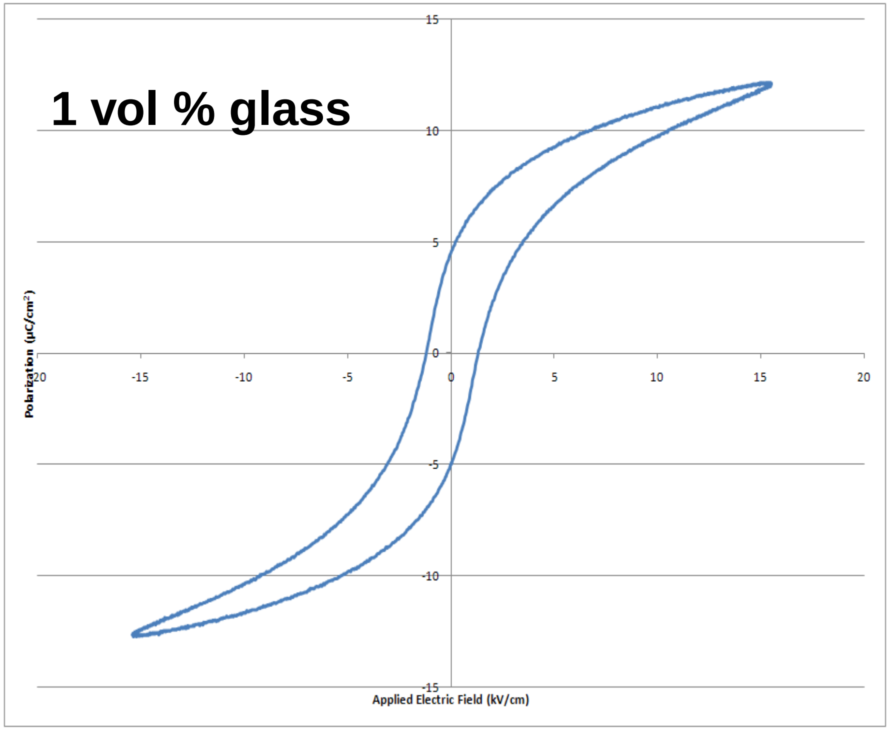
$BaTiO_3$ Nanocomposite High Field Hysteresis





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