Synthesis and Electrical Analysis of Nano-crystalline Barium Titanate and PLZT Nanocomposites

SAND2012-4676P

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Ceramic based nanocomposites have recently demonstrated the ability to provide enhanced permittivity, increased dielectric breakdown strength, and reduced electromechanical strain making them potential materials systems for high energy density applications. A systematic characterization and optimization of barium titanate and PLZT based nanoparticle composites employing a glass or polymer matrix to yield a high energy density component will be presented. This work shows the systematic characterization and optimization of barium titanate and lead lanthanum zirconate titanate nanoparticle based ceramics. The nanoparticles have been synthesized using solution and pH-based synthesis processing routes and employed to fabricate polycrystalline ceramic and nanocomposite based components. The dielectric/ferroelectric properties of these various components have been gauged by impedance analysis and electromechanical response.

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Why Nanoparticle Synthesis??

- Improve the manufacturing and performance of ceramic materials using nanoparticle precursors – nano-enabled technology
- Example: Capacitors are often the largest component in the device.
  - *Reduce the cost* of current ceramic capacitors
  - *Reduce the size* of current ceramic capacitors
- Reduced capacitor size provides both footprint and weight reductions of the device.
- Nanoparticle precursors can potentially lead to lower temperature sintering and allow for easier integration into a monolithic device.
- Development of an engineered glass-polymer-ceramic nanocomposites
  - Decreased sintering temperatures and time
  - Increase in the dielectric properties, electrical breakdown strength and energy density of the material
  - Increased compatibility with on-chip processing, aerosol deposition, robocasting, etc.
- Aqueous based synthesis process – environmental and cost concerns
- Synthesis – convenient, reproducible, scalable and safe, exact processing control
- Improved electrical performance

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

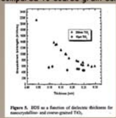
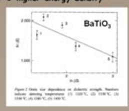
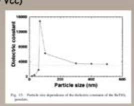


Figure 5. BDS as a function of dielectric thickness for nanocrystalline and coarse-grained TiO_2.



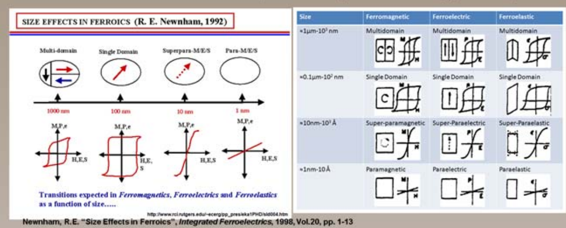
- For ferroelectric (FE) dielectrics, there are additional benefits:
  - Permittivity increases with decreasing grain size down to a critical size dimension (higher energy density)
  - High frequency performance improves with decreasing grain size (maintain permittivity and low loss to higher frequencies)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



Ying and Hsieh, *Mater. Sci. Eng., B* **130** 241 (2007)   Wada et. al., *Jpn. J. Appl. Phys.* **42** 6188 (2003)
Ye et. al., "Influence of nanocrystalline grain size on the breakdown strength of ceramic dielectrics", 2003   Turkasin and Rujjanaul, *J. Mater. Sci. Lett.* **16** 1787 (1996)

Potential exploitation of size effects in ferroics

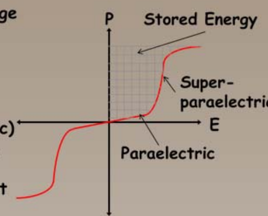
- Efforts on nanoparticle systems to optimize and exploit size effects that could result in enhanced permittivity and/or energy density



Newnham, R.E. "Size Effects in Ferroics", *Integrated Ferroelectrics*, 1998, Vol.20, pp. 1-13

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

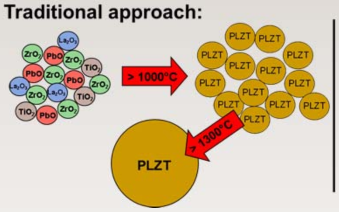


Materials Approach

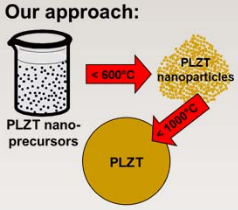
Approach:

- 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:

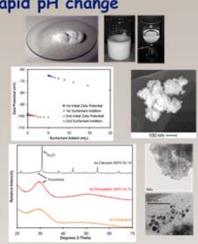


Our approach:

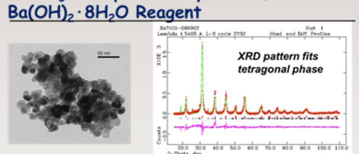


Scalable aqueous PLZTsynthesis route by precipitation via rapid pH change

- $Pb(NO_3)_2 + ZrO\text{-}(NO_3)_2$
- La_2O_3 dissolved in HNO_3
- diluted Ti-O-Pr
- ammonium hydroxide to rapidly raise the pH
- wash, centrifuge, and filter precipitate
- dry amorphous precipitate with large surface area
- Precipitate is weakly agglomerated and may be dispersed through high power sonication
- Amorphous precipitate forms a "proto-pyrochlore" phase then converts to phase pure PLZT
- Crystallite size is reliably <100 nm - dry powder is agglomerated



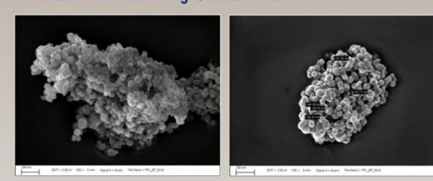
BaTiO$_3$ Nanoparticle Synthesis, Ba(OH)$_2$·8H$_2$O Reagent



- $Ba(OH)_2\cdot 8H_2O$ 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)

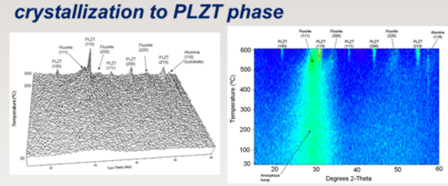
Commercial BaTiO$_3$ from TPL



- 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

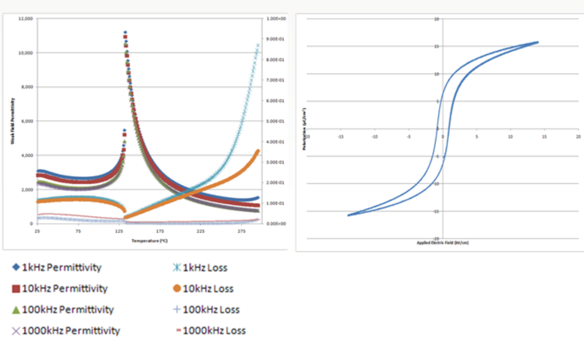
- *TPL, Inc., 3921 Academy Parkway North NE, Albuquerque, NM 87109*

In situ high temperature analysis reveals crystallization to PLZT phase



- Rapid pH-induced precipitation synthesis produces an amorphous powder that converts to fluorite and PLZT upon heating.
- Residual fluorite phase still present at 600°C indicating some second phase present.
- Nanoscale starting materials with nearly atomic homogeneity will achieve phase purity at lower temperatures.
- Synthesis modifications has improved the kinetics and increased the reaction times.

BaTiO$_3$ Weak-Field Permittivity and Hysteresis Behavior Analysis



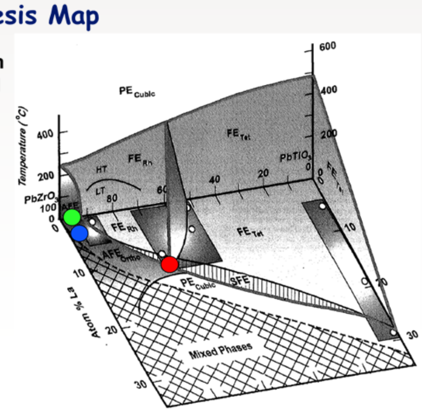
PLZT Synthesis Map

- Phase diagram of the PZT and PLZT solid-solution systems:

– 88/12/70/30

– 100/0/95/5

– 97/3/95/5



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