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

Todd C. Monson, Chris B. Diantonio, Michael R. Winter, Dale L. Huber, Alex W. Roesler, Tom P. Chavez, Tyler E. Stevens, Benjamin D. Fellows, Erika J. Cooley

tmonson@sandia.gov

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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
Benefits of Nanocrystalline Dielectrics

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

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


Figure 5. BDS as a function of dielectric thickness for nanocrystalline- and coarse-grained TiO$_2$.

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.
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)


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/cm³

BTO in iso-PP: 9 J/cm³

- 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

Wang (PSU)

Lanagan (PSU) and Marks (NWU)
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 \( \Rightarrow \) higher energy density

**Volume mixing law:** \[ \log \varepsilon = v_1 \times \log \varepsilon_1 + v_2 \times \log \varepsilon_2 \]

**Energy Density:** \[ \text{EnergyDensity} = \frac{1}{2} \varepsilon_0 \varepsilon_r E^2 \]

Assumptions:
10% glass by volume, \( \varepsilon_r=3 \)
90% BaTiO\(_3\) by volume, \( \varepsilon_r=8000 \)
\( \Rightarrow \) \( \varepsilon_{\text{eff}} = 3635 \)
• 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
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
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

![Silica in epoxy dielectric graph](image)

- Roy, 2005
- Breakdown Strength, kV/mm
- Probability of Failure, %
- Weight Parameter, (log(1/(1-F))
- nm silica + functional groups
- Base polymer
- µm silica

![Graphs and data points](image)
Transitions expected in *Ferromagnetics, Ferroelectrics* and *Ferroelastics* as a function of size.....
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:

> 1300°C

> 1000°C

< 600°C

< 1000°C

PLZT

PLZT nanoparticles

PLZT nano-precursors

PLZT
Scherrer equation analysis of XRD data gives a crystallite size of 38.5 nm
While this result was not anticipated, it may facilitate sample fabrication by easing safety issues.
TEM imaging reveals nanocrystalline grains in calcined PLZT
BaTiO$_3$ Nanoparticle Synthesis, Ba(OH)$_2$·8H$_2$O Reagent

- Ba(OH)$_2$·8H$_2$O 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$_2$O addition
- XRD indicates tetragonal phase present when particles synthesized with 0.5 and 0.6 mol H$_2$O

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

- Reheated BTO particles after initial cycle to 1300 °C
- Endotherm at 122.8 °C consistent with BTO Curie temp. (tetragonal $\Rightarrow$ 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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Extra Slides
Glass addition allows the use of a less expensive electrode and reduced lead volatility.

- PLZT Onset = 1185°C
- PLZT+1 v/o Viox Onset = 1055°C
- PLZT+5 v/o Viox Onset = 939°C

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<th>Temperature (°C)</th>
<th>Pt</th>
<th>30 Ag/70 Pd</th>
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<td>&lt; 1280°C</td>
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<tr>
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Exploiting Size Effects for High Energy Density Dielectrics

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

$$KV \approx k_B T$$

Critical size $\sim 30$ nm

SNL BTO nanoparticles prepared from chemical synthesis route


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.
As-dried precipitate shows uniform morphology and no elemental segregation.

Atomic homogeneity is key to achieving a phase-pure PLZT at low calcining temperatures.
• NanOxide HPB-1000 from TPL
• BET surface area of 16.26±0.0669m²/g
• Attrited to BET surface area of 18.65±0.0459m²/g
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$^\circ$C
BaTiO$_3$ Nanocomposite Devices

- 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

0 vol % glass

1 vol % glass

- 1kHz Permittivity
- 10kHz Permittivity
- 100kHz Permittivity
- 1000kHz Permittivity

- 1kHz Loss
- 10kHz Loss
- 100kHz Loss
- 1000kHz Loss
BaTiO$_3$ Nanocomposite
High Field Hysteresis

0 vol % glass

1 vol % glass