Mitigating Breakdown in High Energy Density Perovskite Polymer Nanocomposite Capacitors

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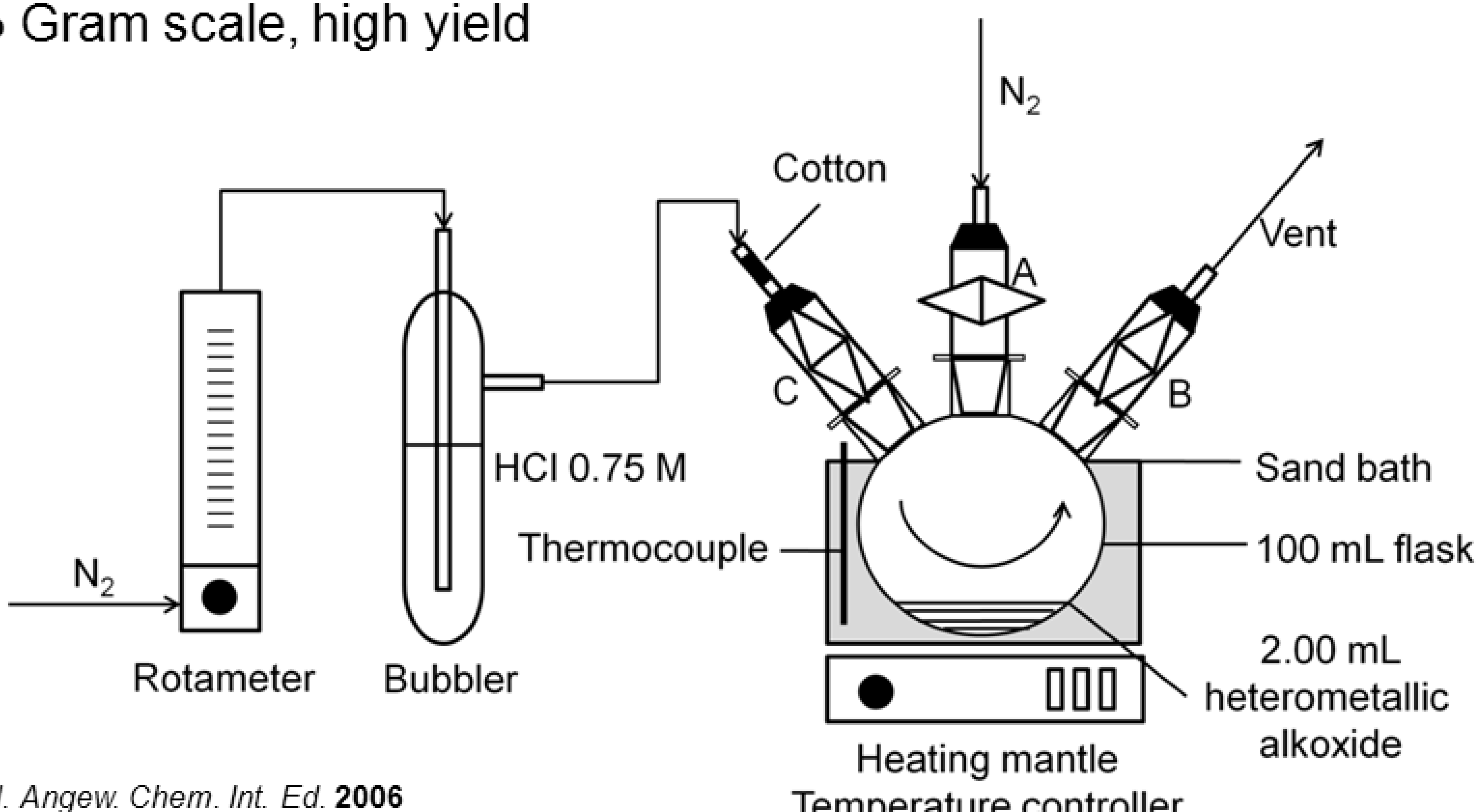
Vapor Diffusion Sol–Gel Synthesis of Perovskite Oxides

$$AB(OC_3H_6OCH_3)_6 + 3\ H_2O_{(g)} \xrightarrow[48\ h]{22\ ^\circ C,\ 1\ atm} ABO_3 + 6\ HOC_3H_6OCH_3$$

A = Sr^{2+}, Ba^{2+} B = Ti^{4+}, Zr^{4+}

- Low temperature, atmospheric pressure, near neutral pH
- Gram scale, high yield



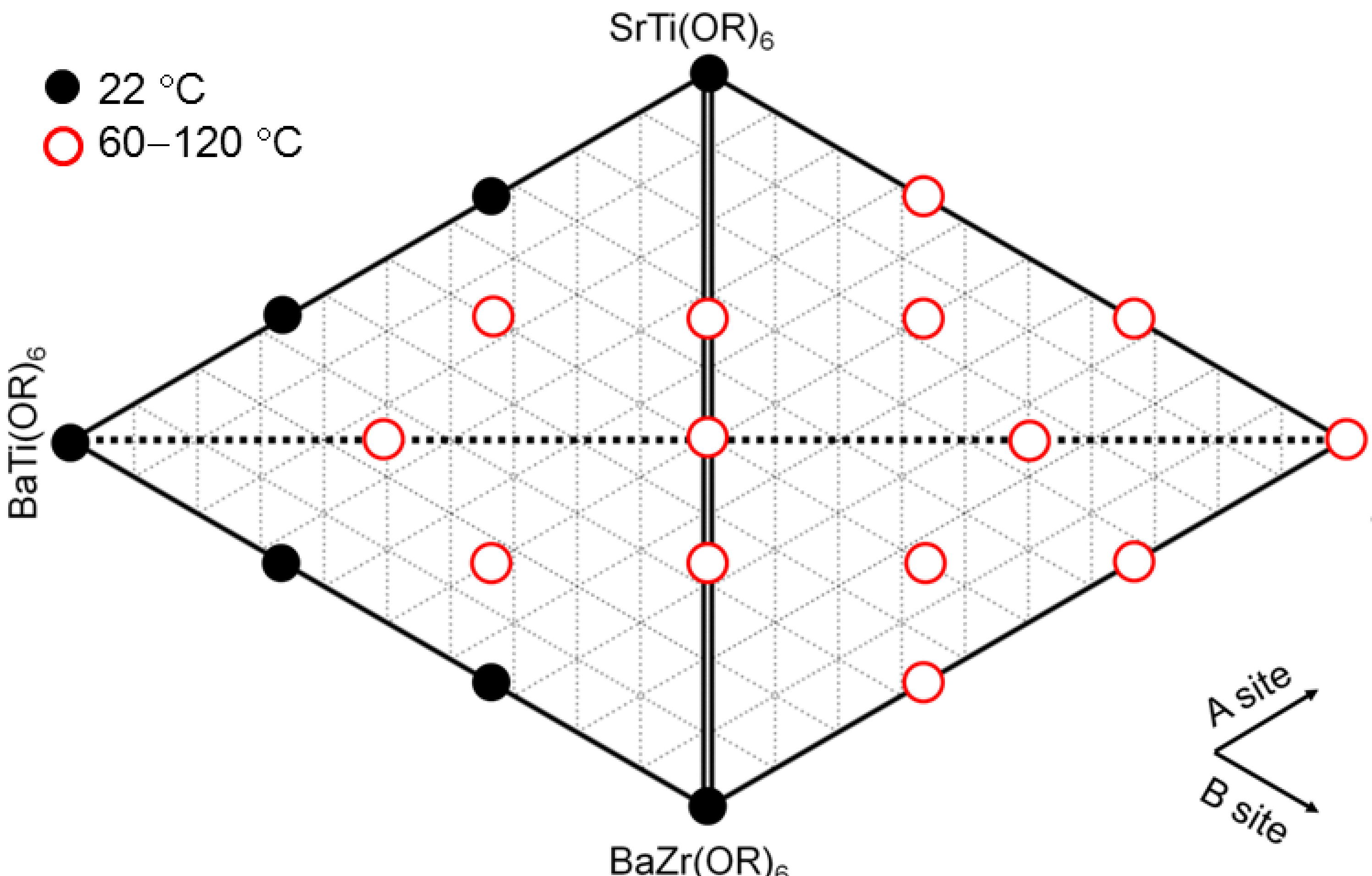
Brutchey *et al*. *Angew. Chem. Int. Ed.* **2006**
Beier *et al*. *J. Mater. Chem*. **2010**
Rabuffetti *et al*. *Chem. Comm*. **2012**

Isovalent Substitution

$$x\,AB(OR)_6 + y\,A'B'(OR)_6 + H_2O_{(g)} \xrightarrow[72\ h]{T,\ 1\ atm} A_xA'_yB_xB'_yO_3 + ROH$$

A, A' = Sr^{2+}, Ba^{2+} B, B' = Ti^{4+}, Zr^{4+}

R = $C_3H_6OCH_3$



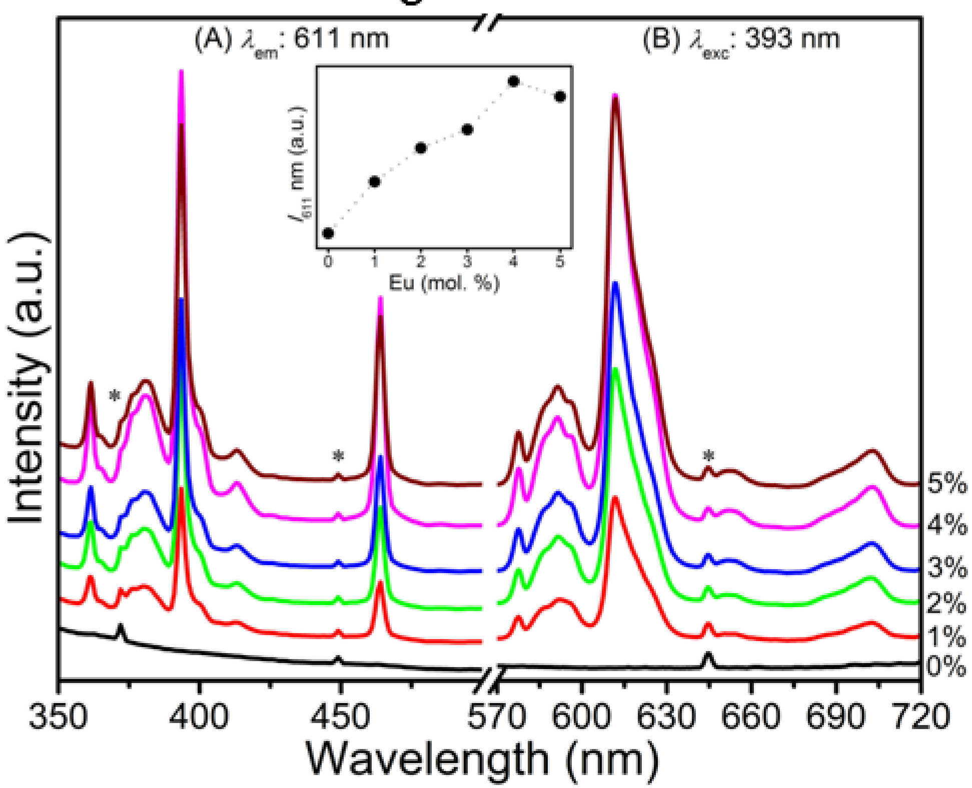
Rabuffetti and Brutchey **2012**, submitted

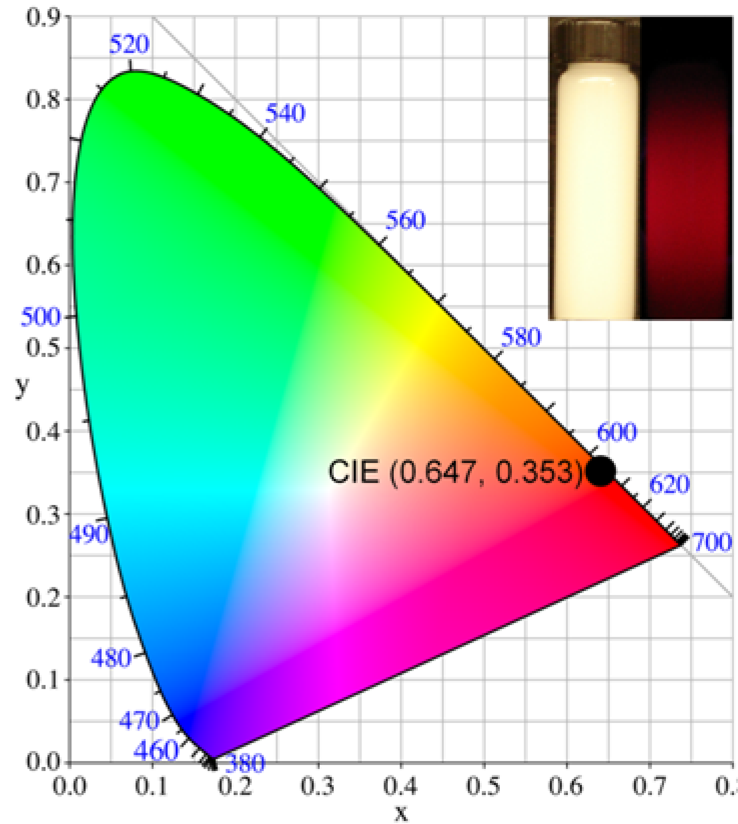
Aliovalent Substitution

$$BaZr(OR)_6 + x\,Eu^{3+} + 3\,H_2O_{(g)} \xrightarrow[48\ h]{22\ °C,\ 1\ atm} x\mathrm{Eu}{:}BaZrO_3 + 6\ ROH$$

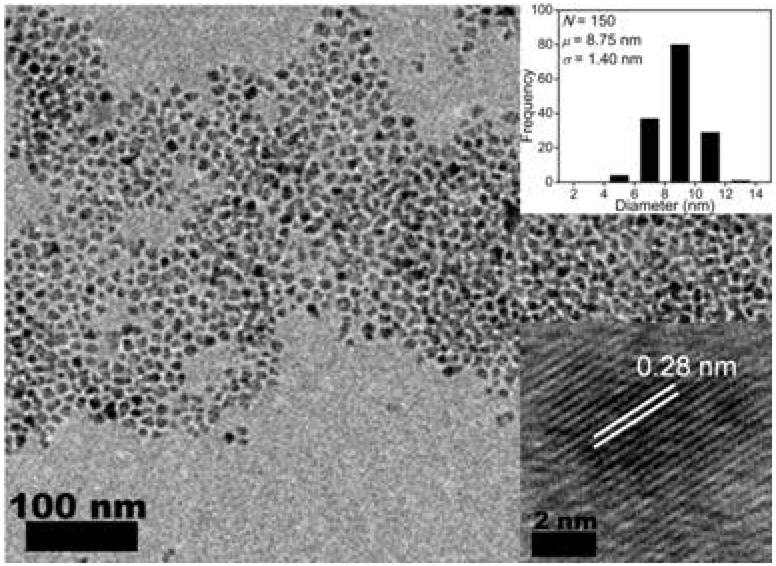
x = 1.0, 2.0, 3.0, 4.0, 5.0 mol. % (nominal)
1.1, 1.8, 2.8, 4.2, 4.8 mol. % (elemental analysis)

Red-to-orange ratio ~ 3.4

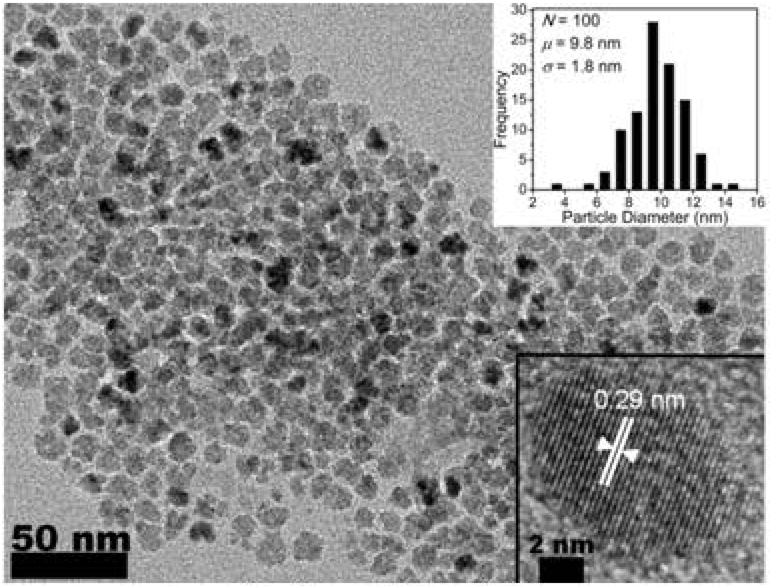




Morphology

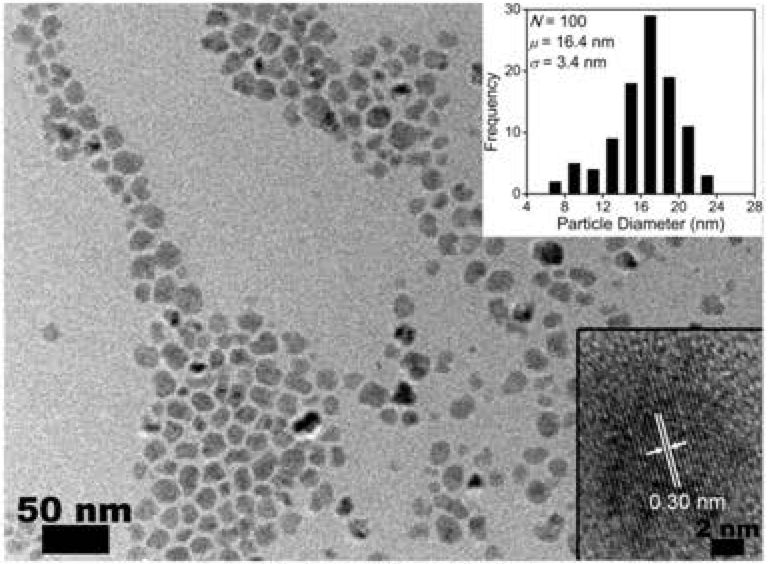


$BaTiO_3$



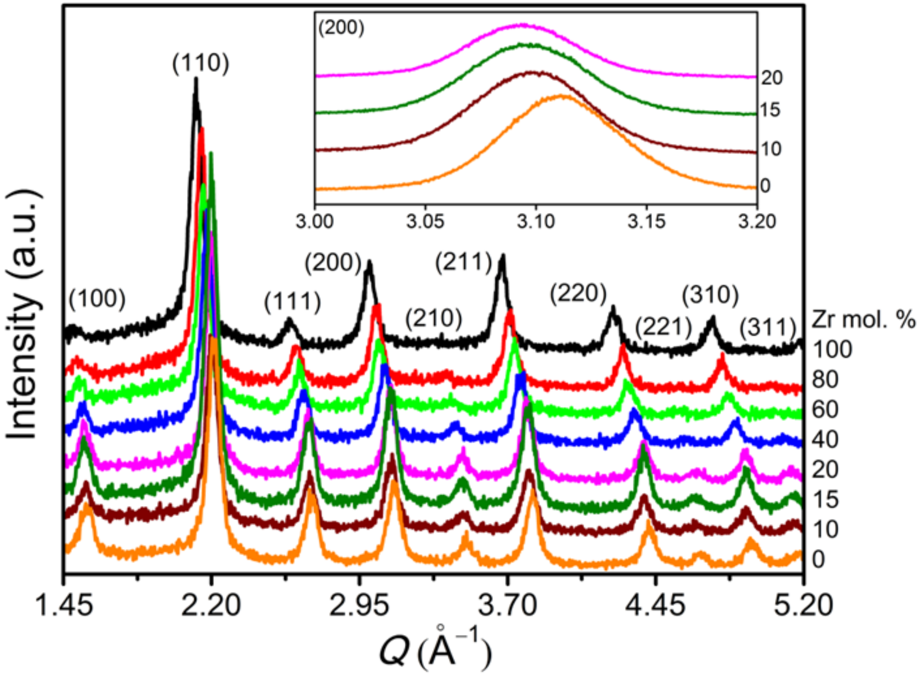
$BaZr_{0.1}Ti_{0.9}O_3$

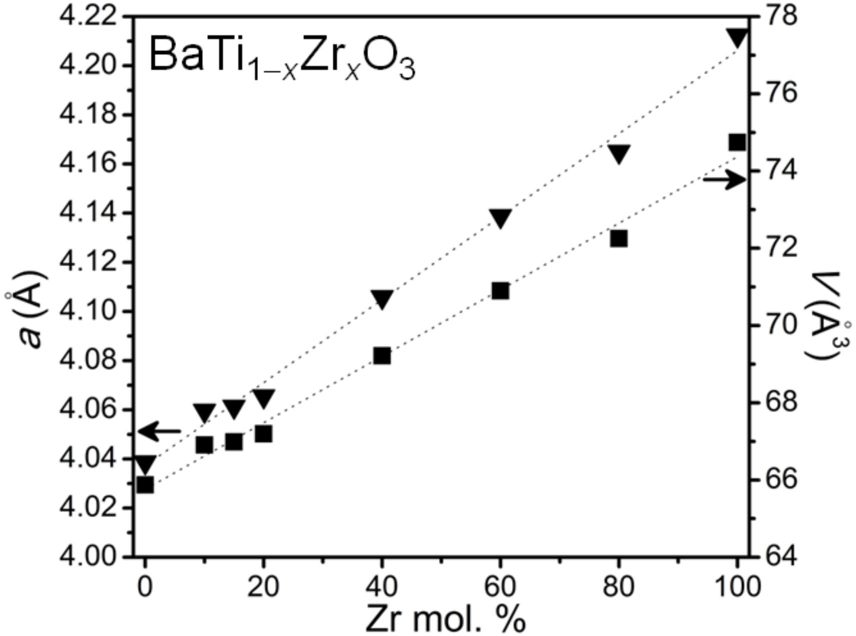
- Sub-10 nm
- Narrow size distribution
- Single crystalline

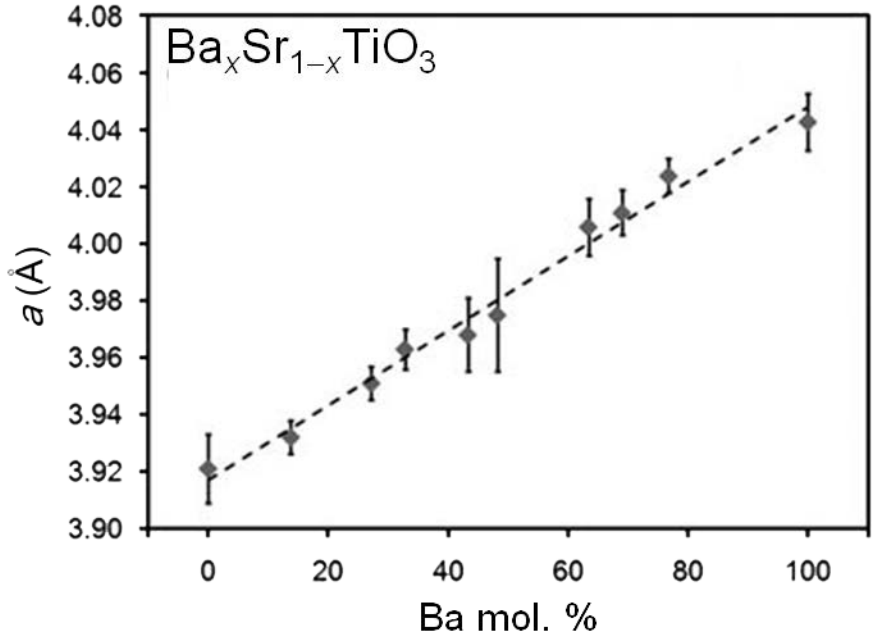


3% Eu:$BaZrO_3$

Crystal Structure



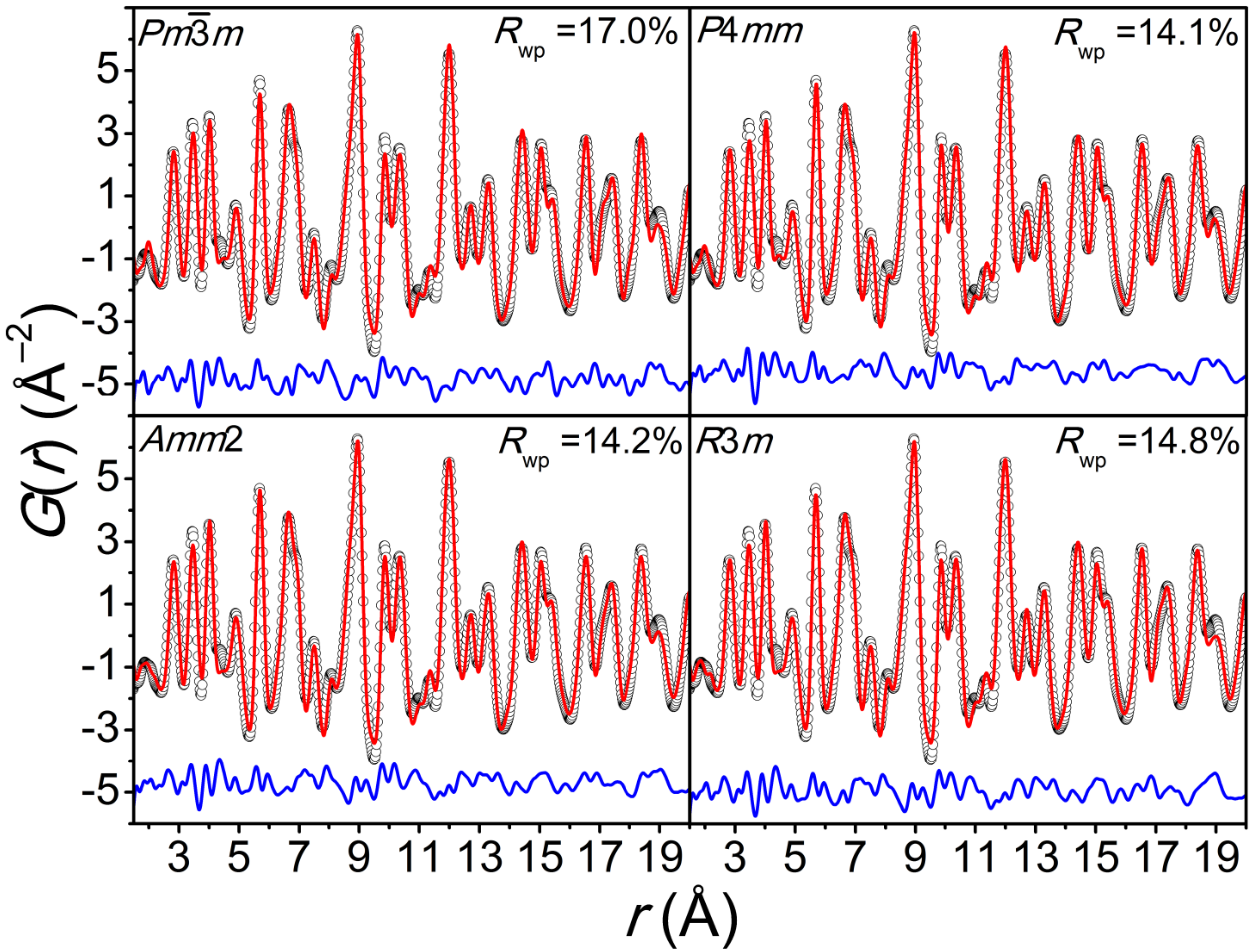




- Crystalline
- Phase pure
- Solid solutions (Vegard's Law)

Local Crystal Structure

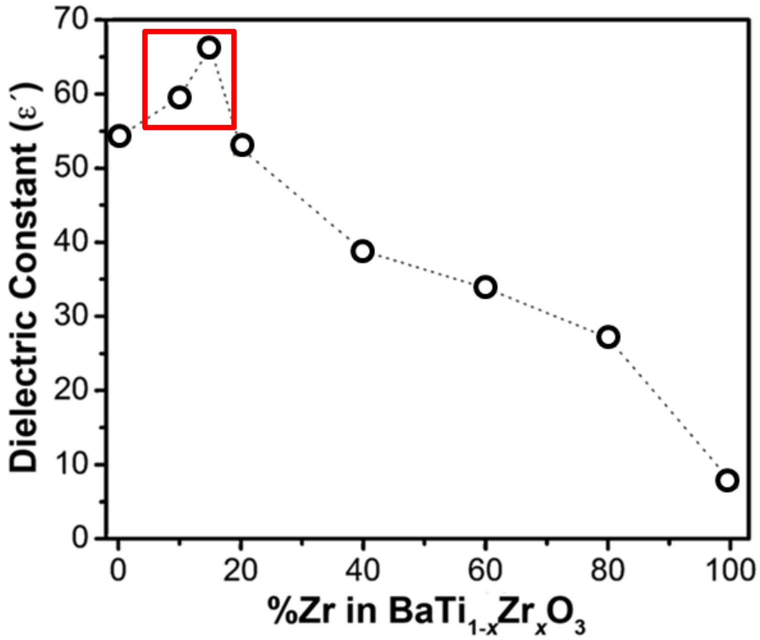
Pair distribution function analysis

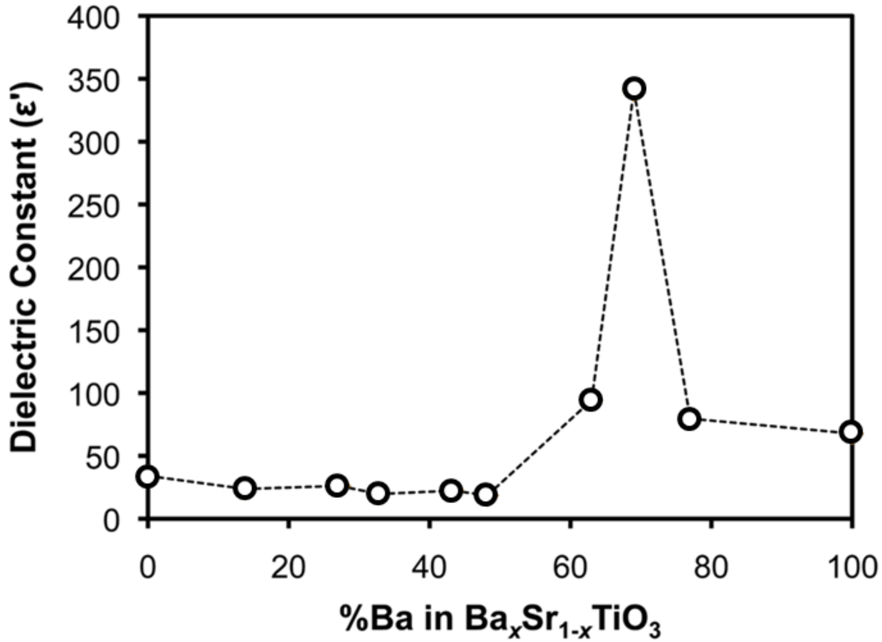


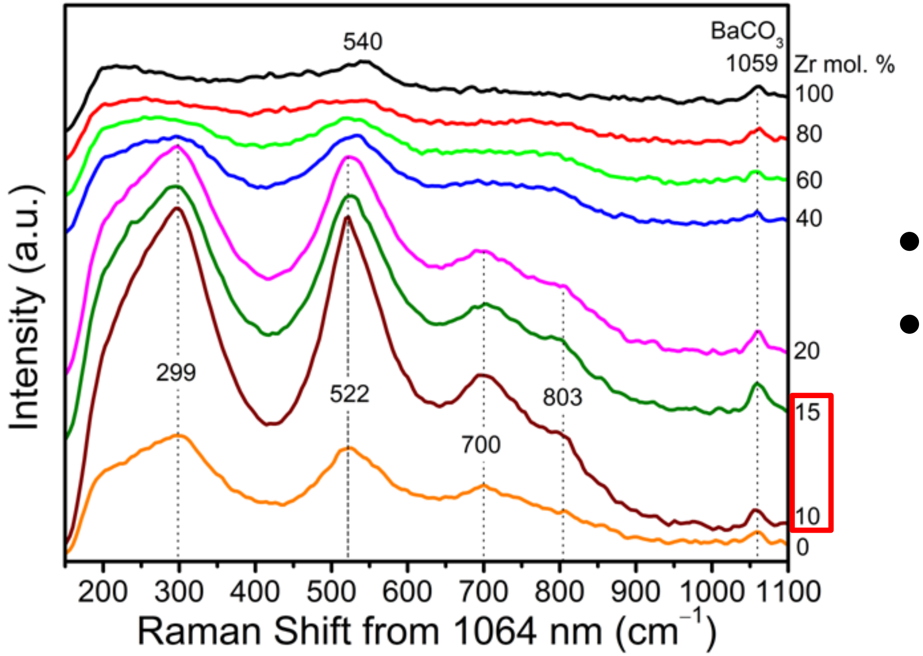
- Ferroelectric nanoregions at room temperature
- Tetragonal and/or orthorhombic local symmetry

Rabuffetti and Brutchey **2012**, submitted

Dielectric Properties

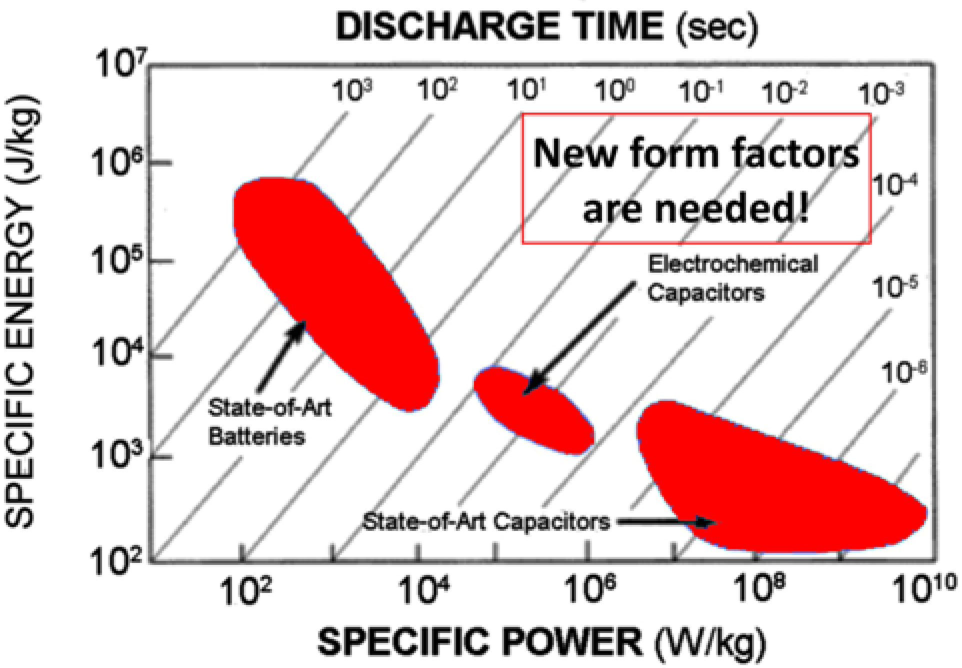


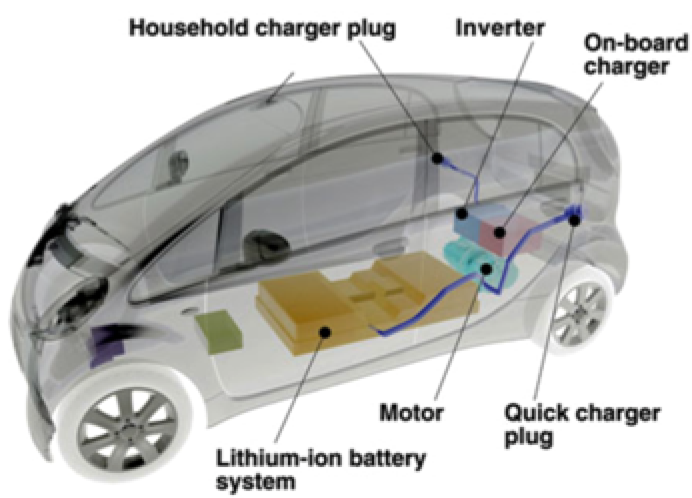




- ε´ maximized via isovalent substitution
- Volume fraction of ferroelectric domains

High Energy Density Nanocomposites





$$D = 0.5\varepsilon'\varepsilon_0 E_{bd}^2 \quad \text{(J/cc)}$$

Polymers:
- High E_{bd} (500 V/µm)
- High frequency stability
- Graceful failure
- ✘ Low ε′ (2-5)

Ceramics:
- High ε′ (>200)
- High T stability
- ✘ Low E_{bd}
- ✘ Catastrophic failure

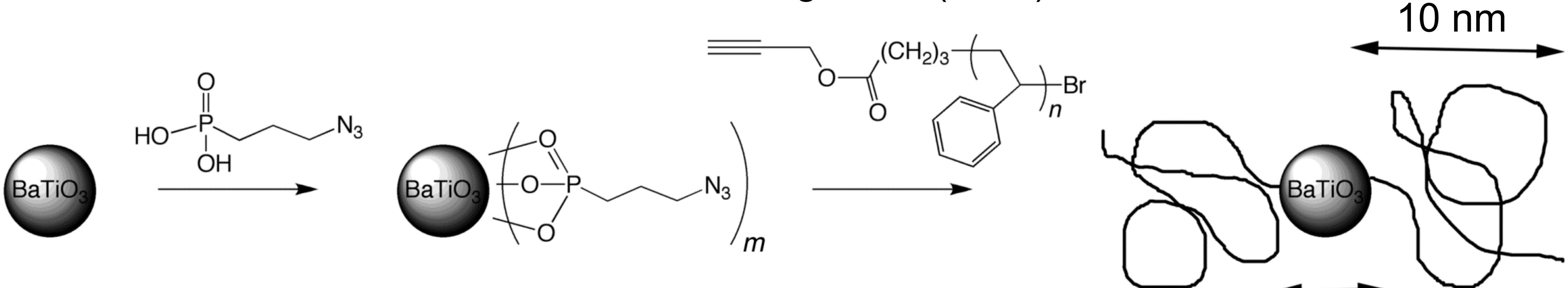
⇩

Ideal Nanocomposite:
- High E_{bd} (>300 V/µm)
- Moderate ε′ (20-50)
- Moderate T stability (T_g >100 °C)
- Low loss (≤1%)

Breakdown strength must be retained past filler percolation threshold.

Surface Functionalization via “Click” Chemistry

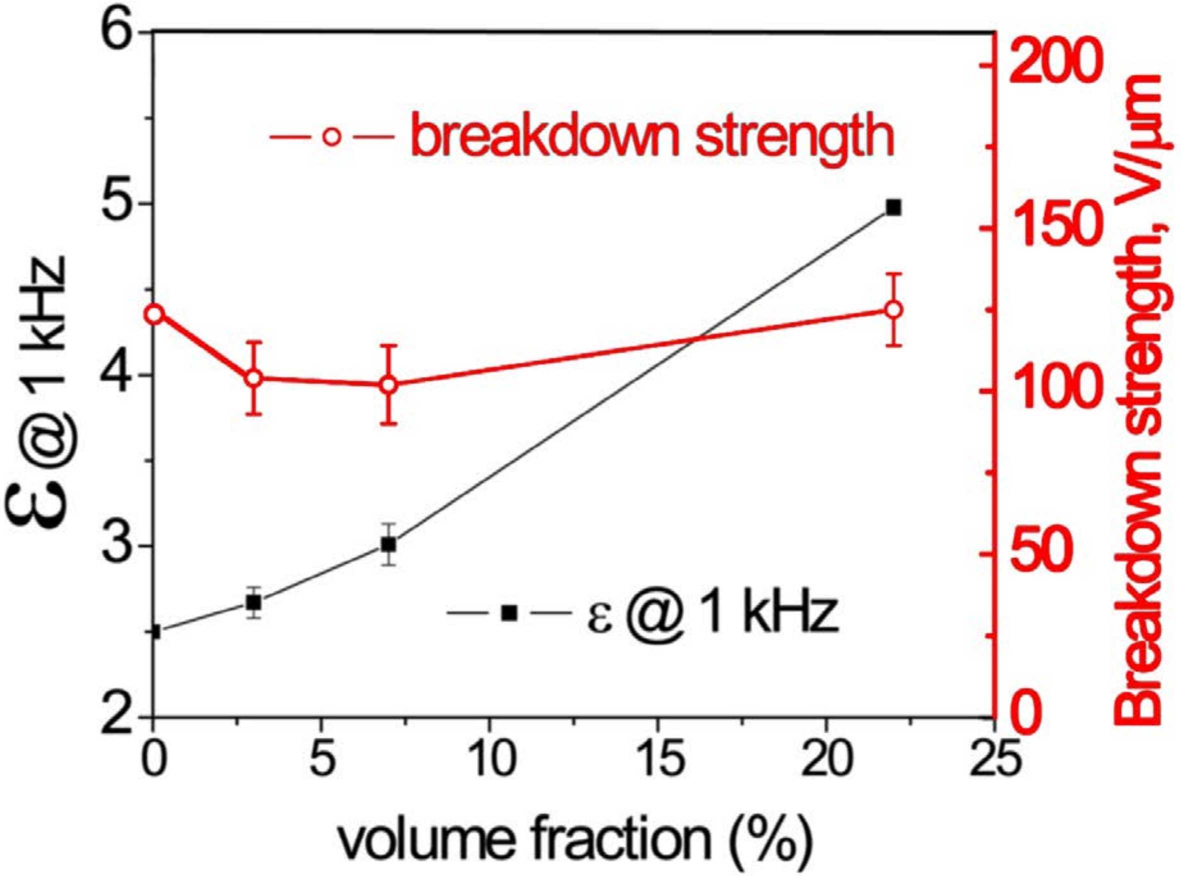
10^5 g mol^{-1} (100k)



Grafting density: 0.38 azide nm^{-2}

Grafting density: 0.022 chains nm^{-2}
2.5 chains per nanocrystal

Mitigating Breakdown by Percolation



Breakdown strength of neat polymer is retained past percolation limit.

with Tchoul, Fillery, Durstock, Vaia (AFRL) **2012,** unpublished

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