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Short-range distortions and long-range cubic order in barium titanate

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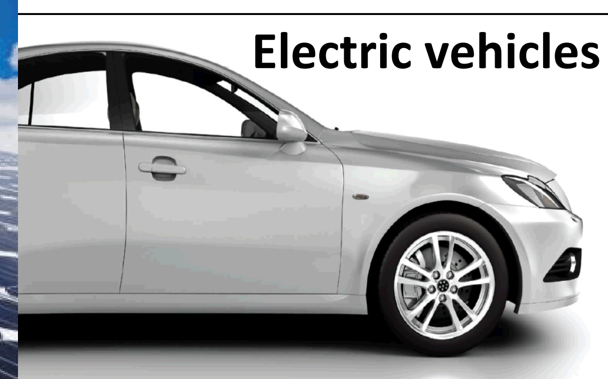
Electrostatic Capacitors are Ubiquitous

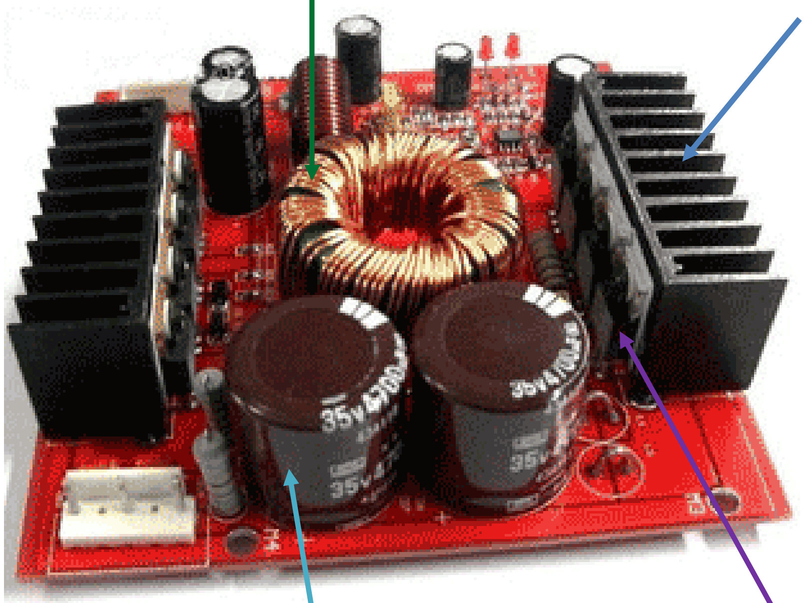


Courtesy of Bob Kaplar

Capacitors Impact Power System Volume and Weight

Passive elements and thermal management comprise the bulk of the volume and mass of a power converter

WBG/UWBG materials enable higher switching frequency and better thermal management

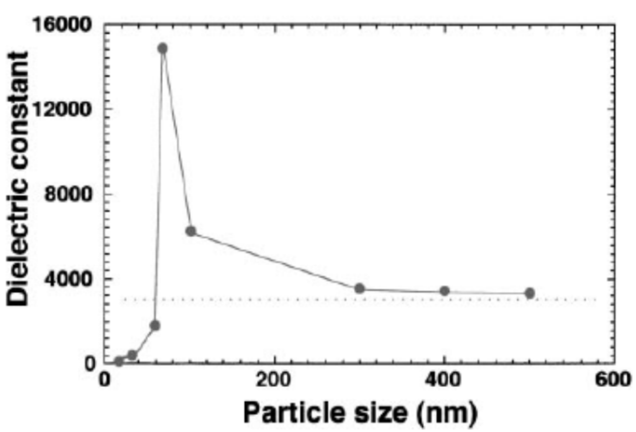


J. Neely, J. Flicker, B. Kaplar

Benefits of Nanocrystalline Ferroelectrics

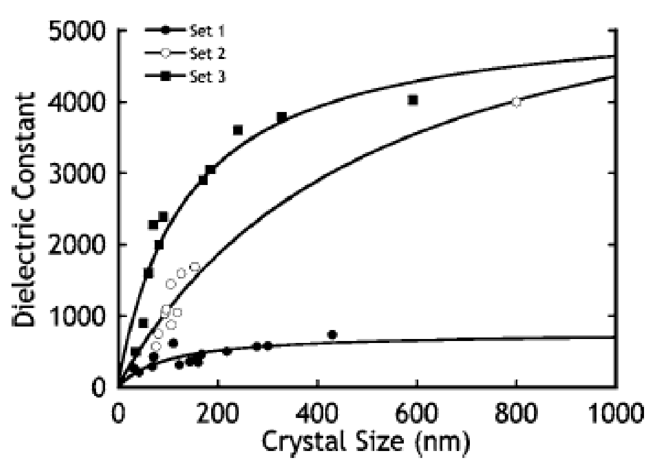
- **Permittivity increases with decreasing grain size down to a critical size dimension (higher energy density)**
- **High frequency performance improves with decreasing grain size (maintain permittivity and low loss to higher frequencies)**
- **Field and temperature dependence of permittivity may improve (i.e. lower TCC and VCC)**

Most widely reported and agreed upon behavior



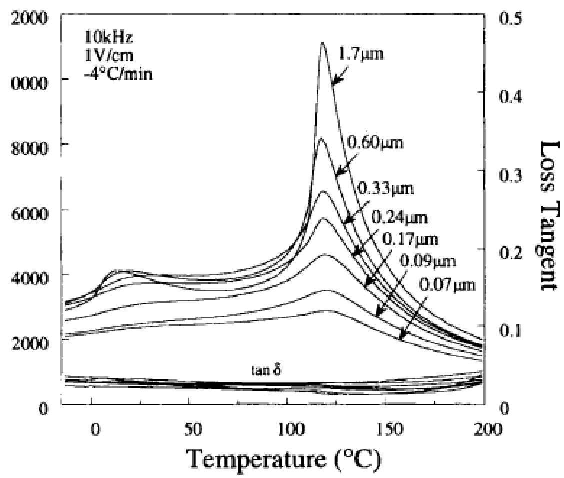
$BaTiO_3$ particles in solution

Wada et. al., Jpn. J. Appl. Phys. Vol. 42 (2003) 6188–6195



Sintered $BaTiO_3$

Aygün et. al., J. Appl. Phys. Vol. 109 (2011) 034108



Frey, et. al., Ferroelectrics, Vols. 206-207, (1998) 337-353

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Benefits of Nanocrystalline Ferroelectrics

- **Nanocrystalline grain size provides high breakdown strength (BDS)**
- **Lower field-induced strain (i.e., better electromechanical performance)**

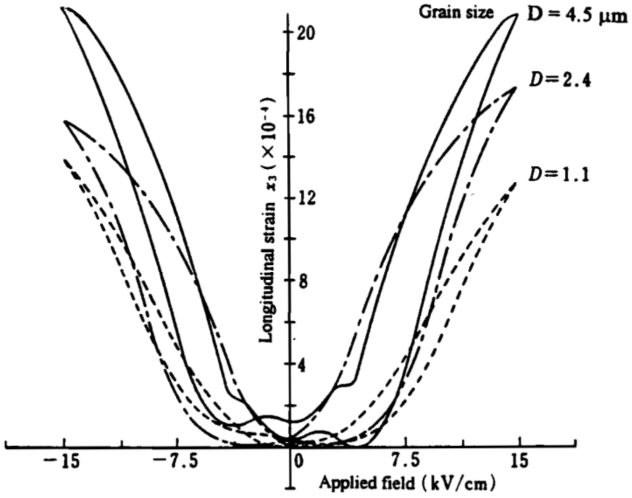

Fig. 3.28 Grain size dependence of the induced strain in PLZT ceramics.

from Kenji Uchino's book, Ferroelectric Devices

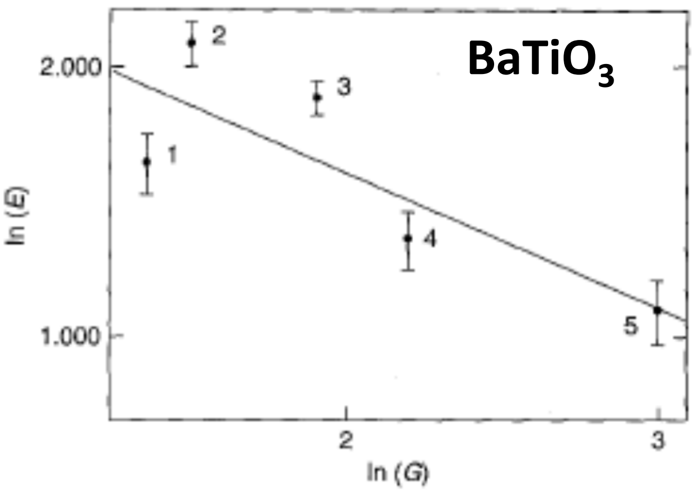

Figure 2 Grain size dependence on dielectric strength. Numbers indicate sintering temperatures: (1) 1320 °C, (2) 1330 °C, (3) 1350 °C, (4) 1380 °C, (5) 1400 °C.

TUNKASIRI, JOURNAL OF MATERIALS SCIENCE LETTERS 15 (1996) 1767-1769

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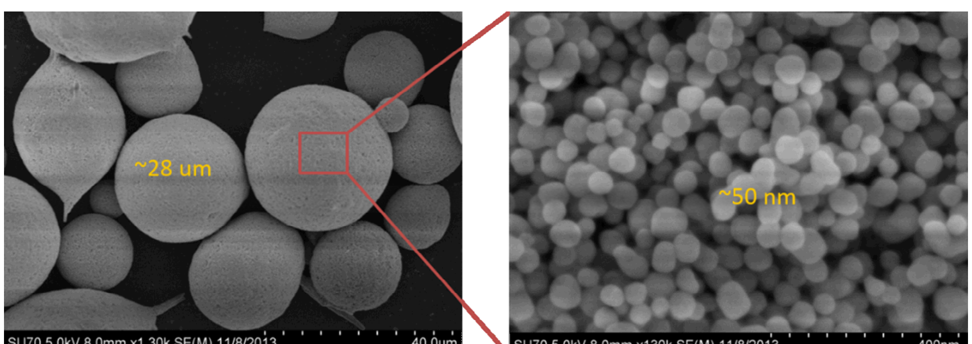
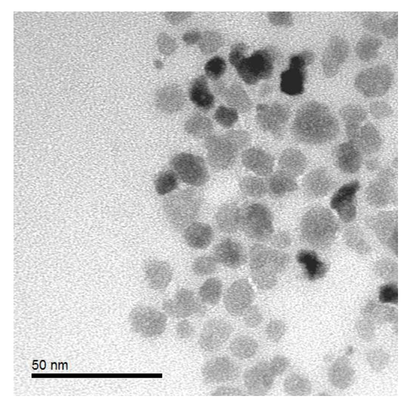
$BaTiO_3$ (BTO) Nanoparticles Studied

Source	Name	Primary Particle Diameter (nm)	Synthesis Method
Sandia	SNL	10	80°C solution
Sakai	KZM-50	50	hydrothermal
Sakai	BT-01	100	hydrothermal
Sakai	BT-02	200	hydrothermal
Sakai	BT-03	300	hydrothermal
Sakai	BT-04	400	hydrothermal
Sakai	BT-05	500	hydrothermal



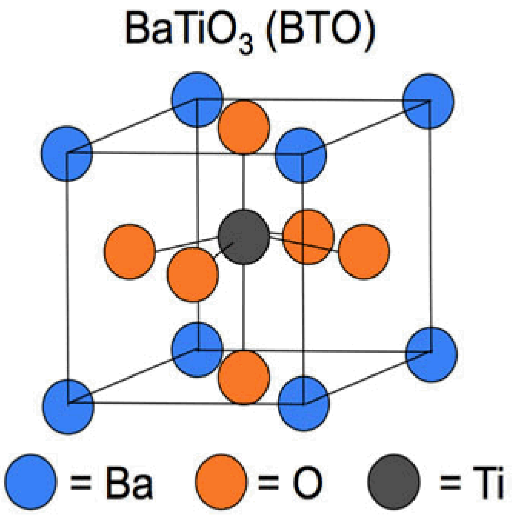
Sakai KZM-50



Sandia solution synthesized $BaTiO_3$

Preview of results

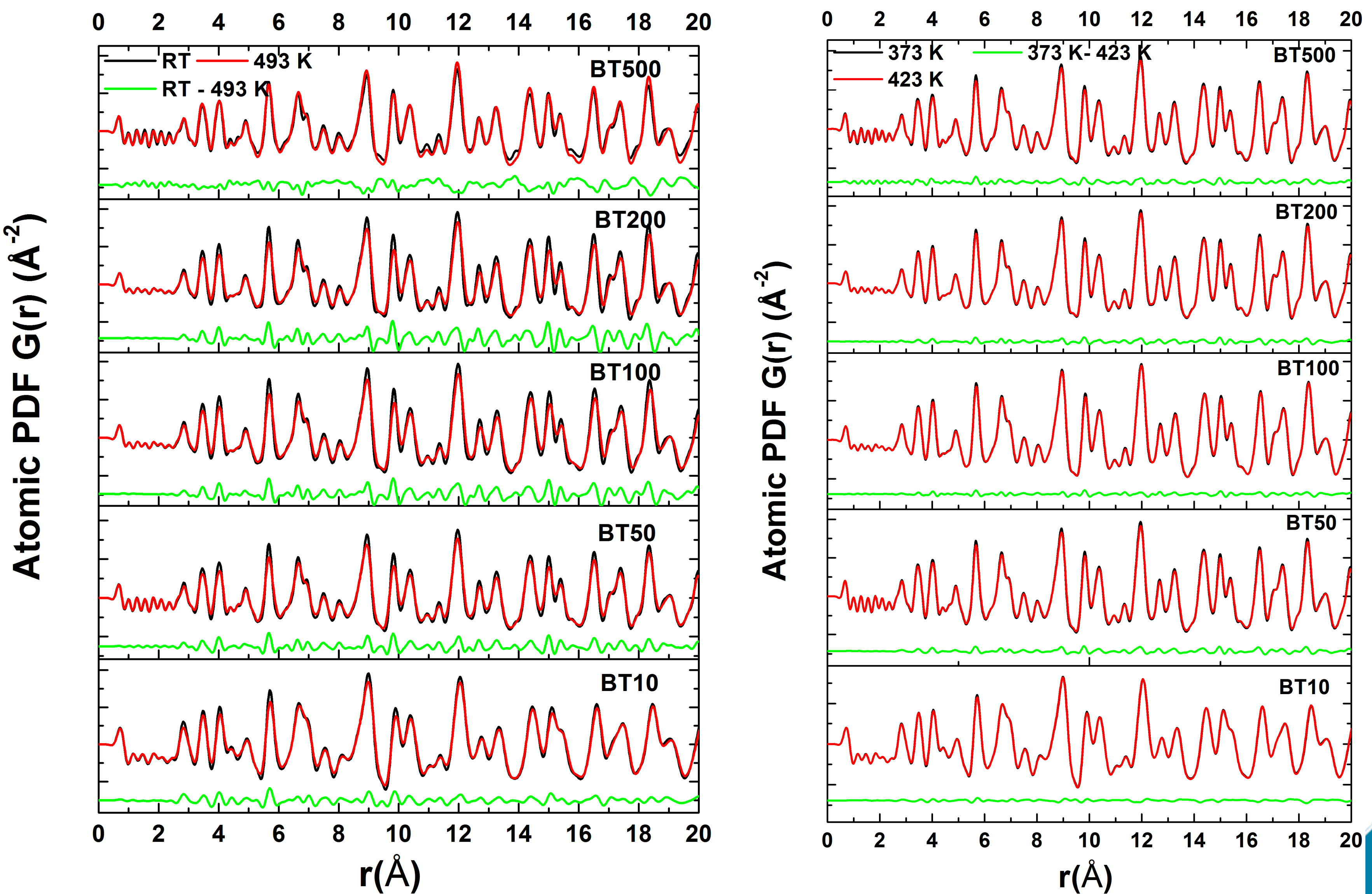
- **ALL particle sizes show ~ 0.1 Å Ti displacements at ALL temps: 20° to 200°C !**
- **Large (> 200 nm) BTO NPs (bulk) exhibit a sharp structural transition at 120°C**
- **Small (< 200 nm) BTO NPs exhibit instead a gradual crossover with increasing temp.**



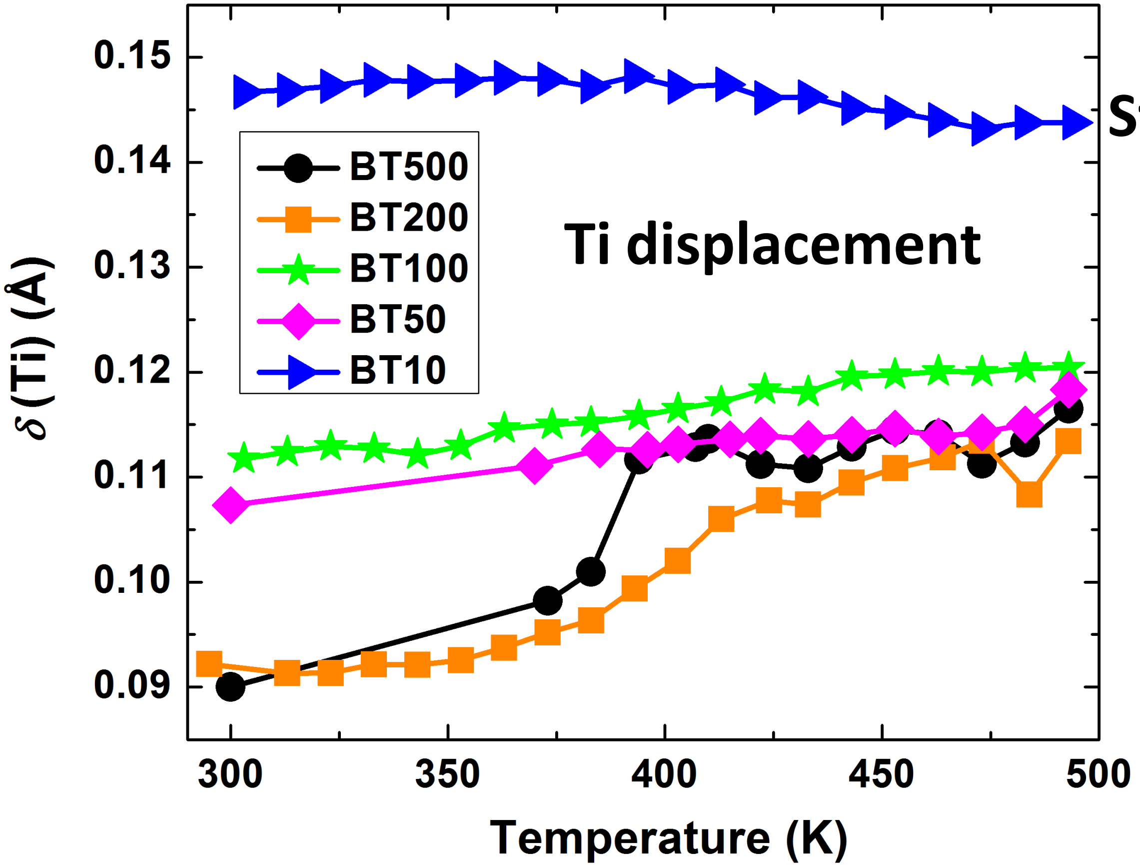
< 120 °C Tetragonal (Ferroelectric)

> 120 °C Cubic (Paraelectic)

aPDF Temperature Dependence



Fits to PDFs over 60 Å



Structural fitting parameters:

Tetragonal model:

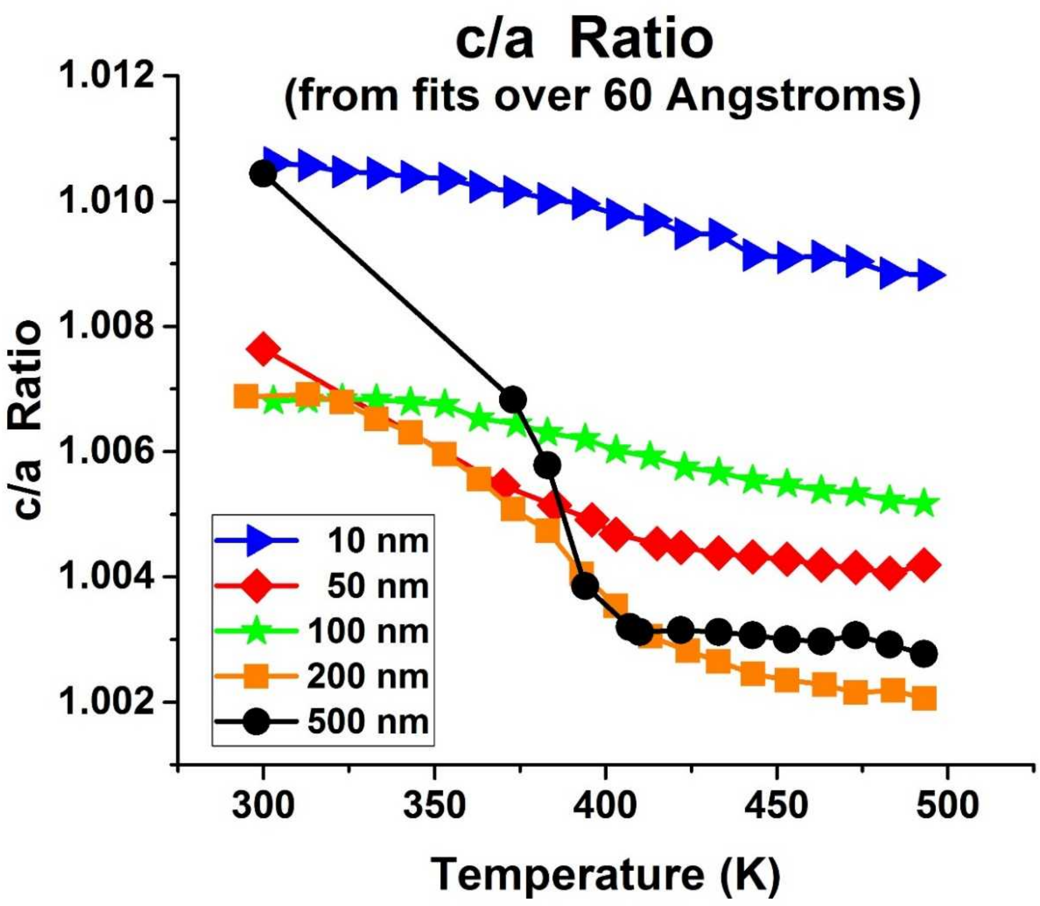
a, c, $Ti_{\delta z}$

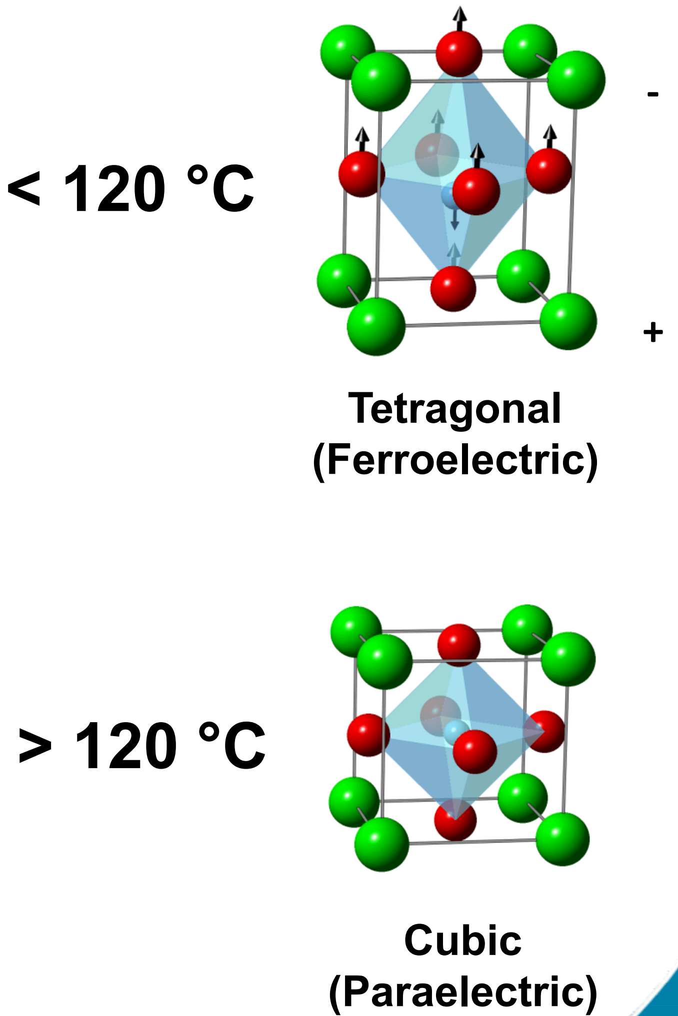
U_{iso} for Ti, Ba, O

Cubic model:

a, U_{iso} for Ti, Ba, O

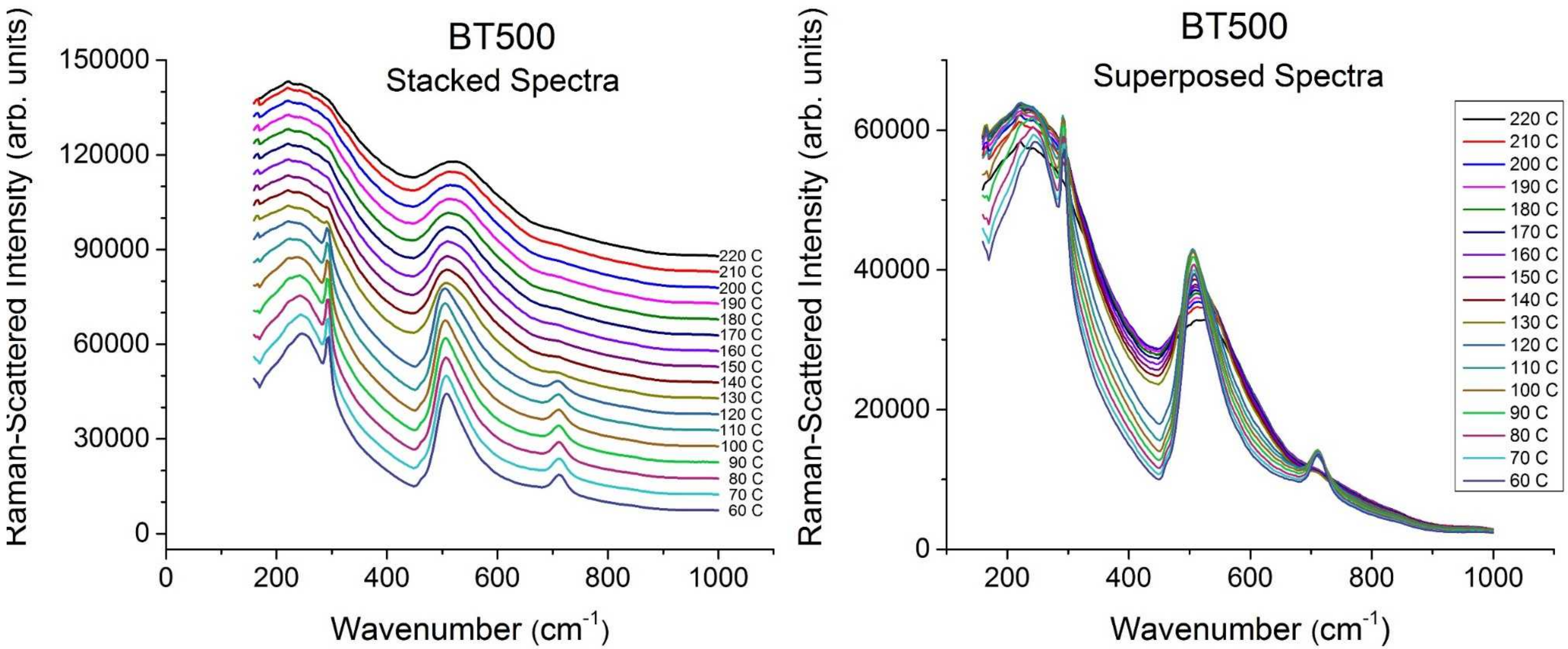
Tetragonal c/a Ratio vs. Temperature





Raman Scattering from the 500 nm BTO NPs

Tetragonal Raman lines disappear abruptly at 120°C !



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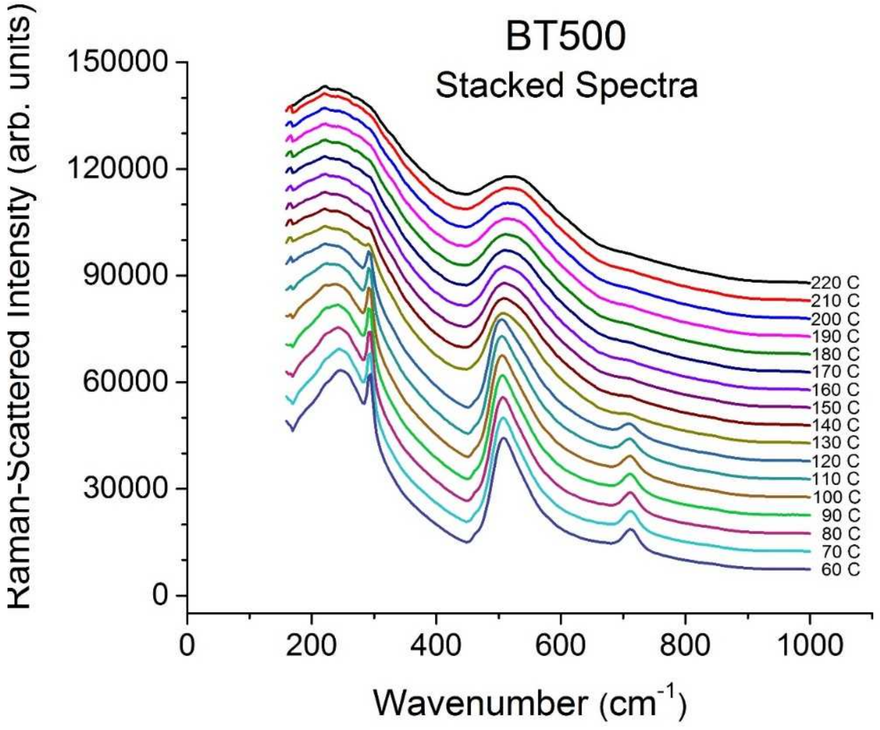
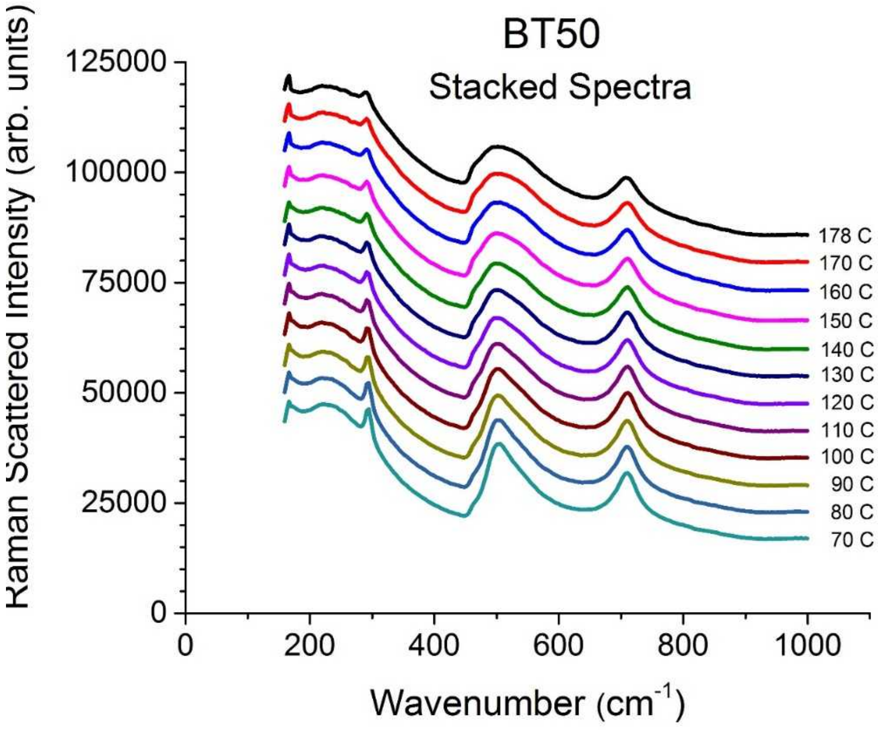
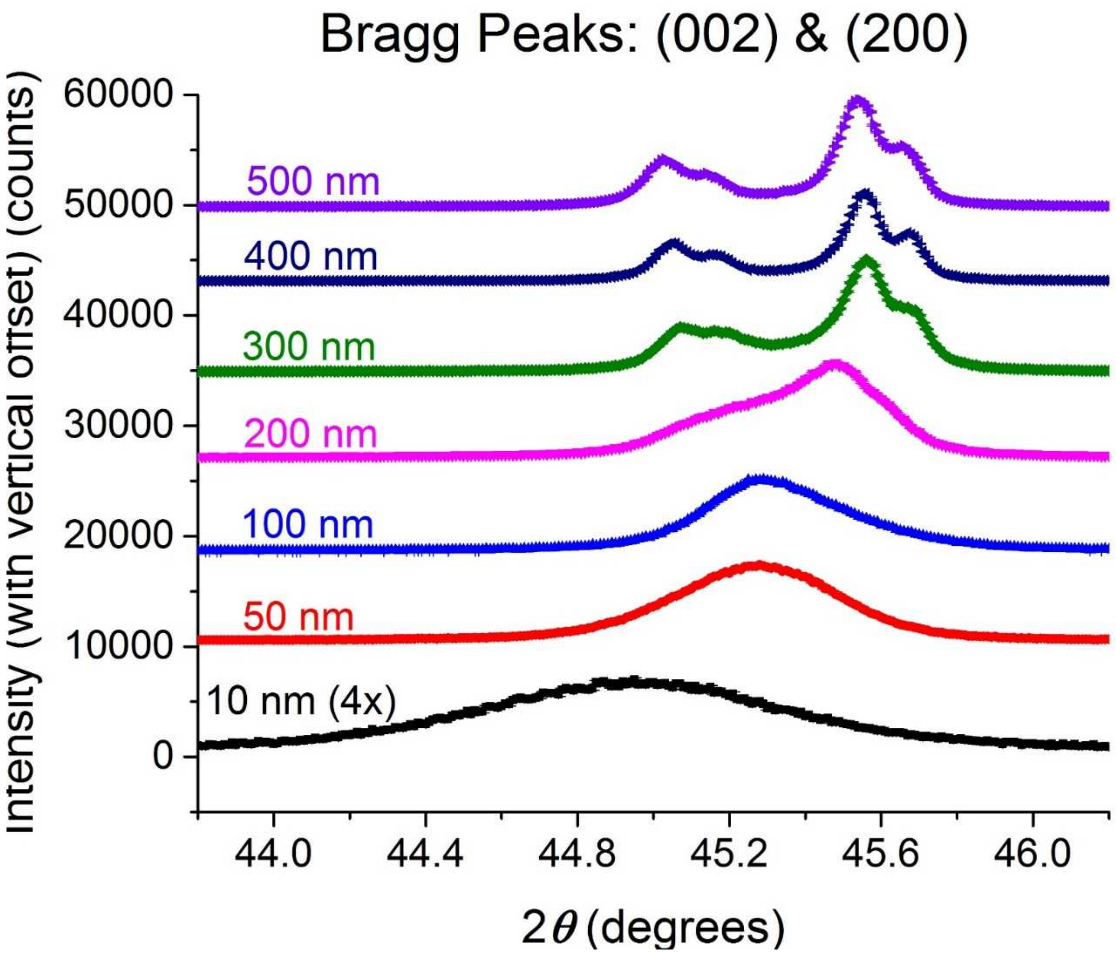
500 nm & 50 nm Raman Comparison

Tetragonal Raman lines for 50 nm BTO NPs persist above 120°C !





XRD Bragg Peaks @ Room Temperature

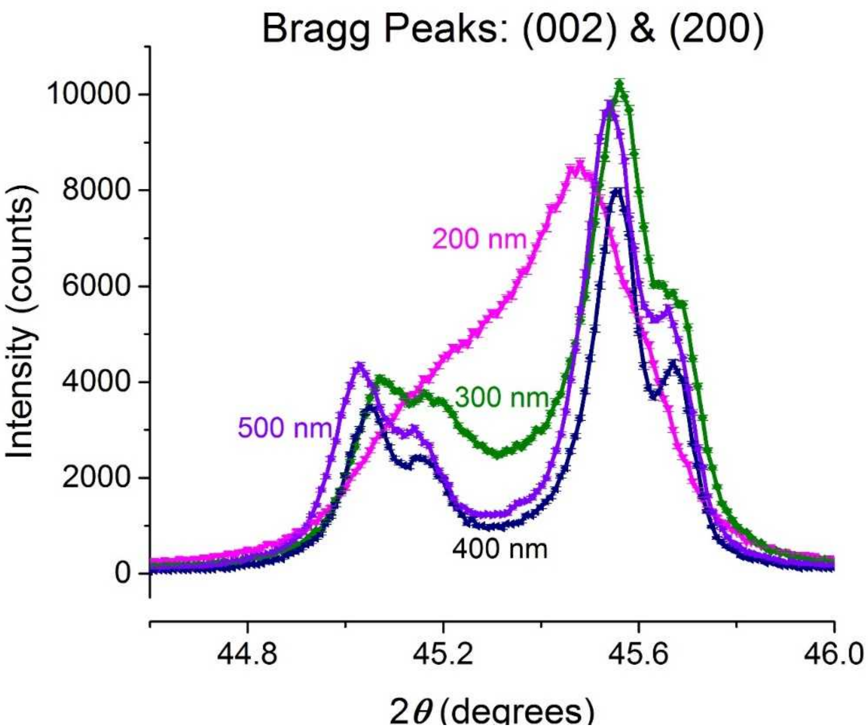


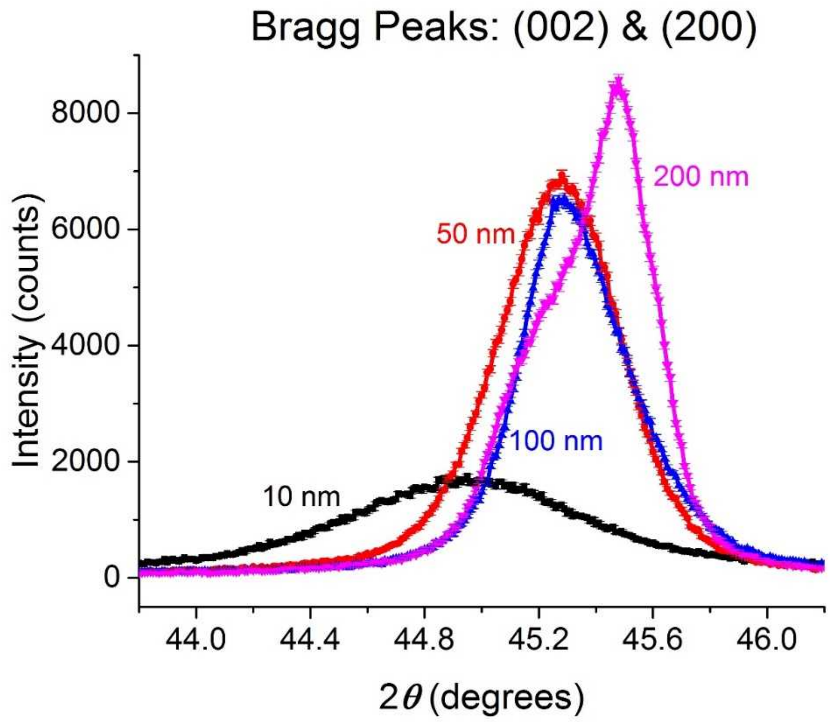
Large BTO NPs (bulk) have split peaks!

Small BTO NPs have singlet peaks!

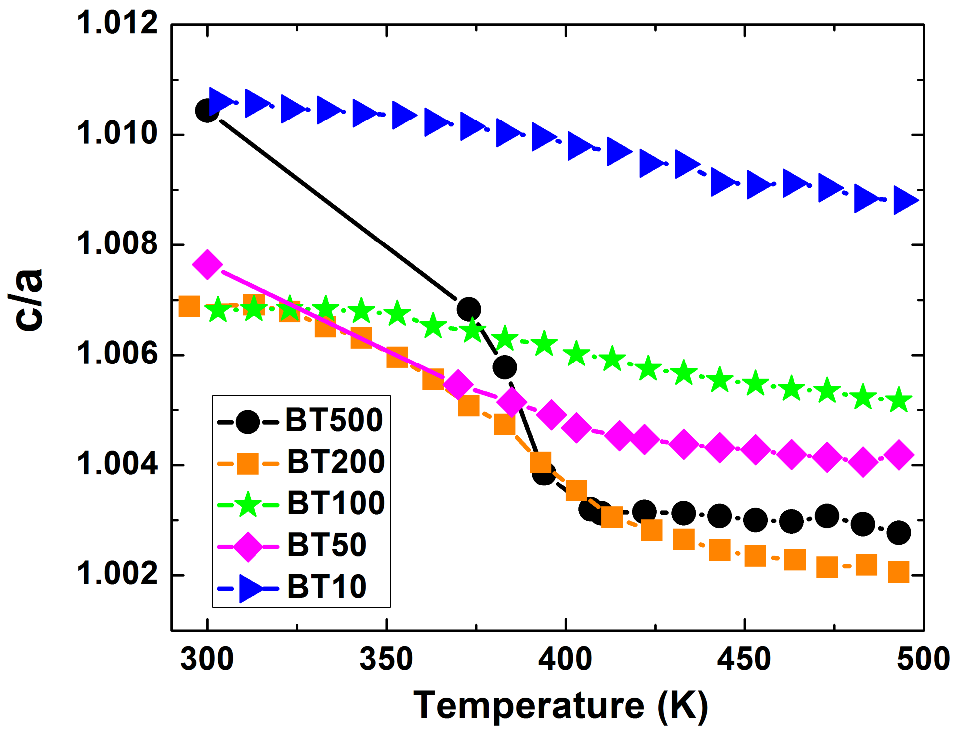
200 nm BTO NPs are on the fence!

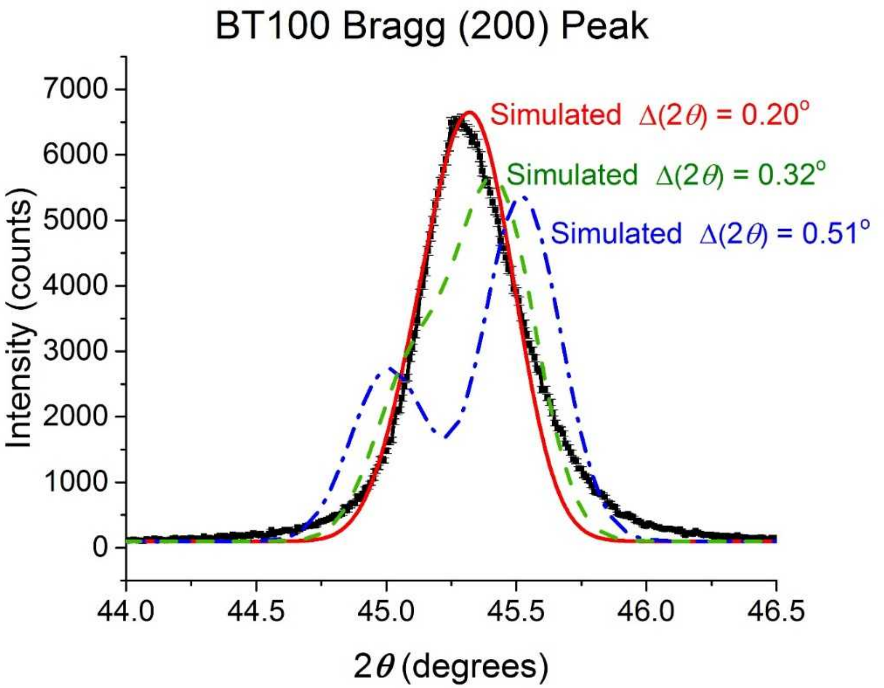
Bragg Peaks for Small & Large BTO NPs





Reduced c/a Ratios Account for Bragg Peak Singlets!





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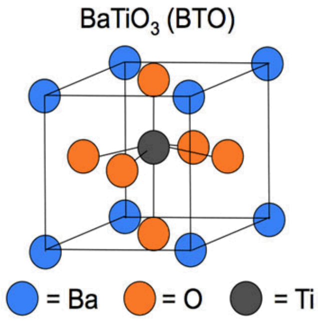
Conclusions

<u>ALL</u> particle sizes show ~ 0.1 Å Ti displacements at <u>ALL</u> temps: 20° to 200°C !

- **Large (> 200 nm) BTO NPs (bulk) exhibit a sharp long-range c/a decrease @ 120°C**
- **Low c/a wipes out tetragonal Raman lines above 120°C**
- **Low c/a yields Bragg peak singlets above 120°**

- **Small (< 200 nm) BTO NPs exhibit a gradual c/a decrease with increasing temp.!**
- **Decreasing c/a allows tetragonal Raman lines but with decreasing amp.!**
- **Decreasing long-range c/a yields small Bragg splittings → singlets!**



Acknowledgements

- The authors wish to thank Dr. Susan Heidger of the Air Force Research Laboratory/High Power Microwave Division for significant support of this work.
- We thank Renee M Van Ginhoven of AFRL/RDHE for many valuable discussions

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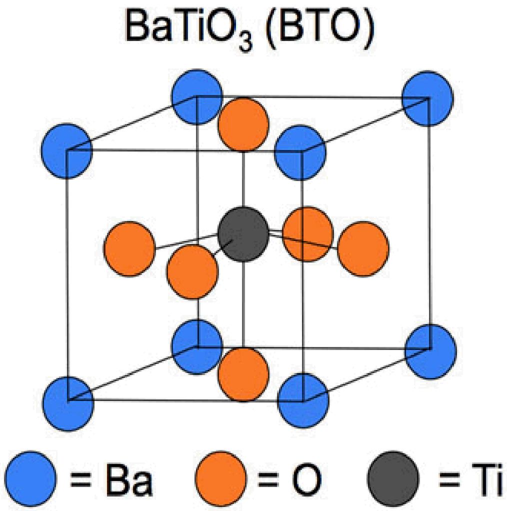
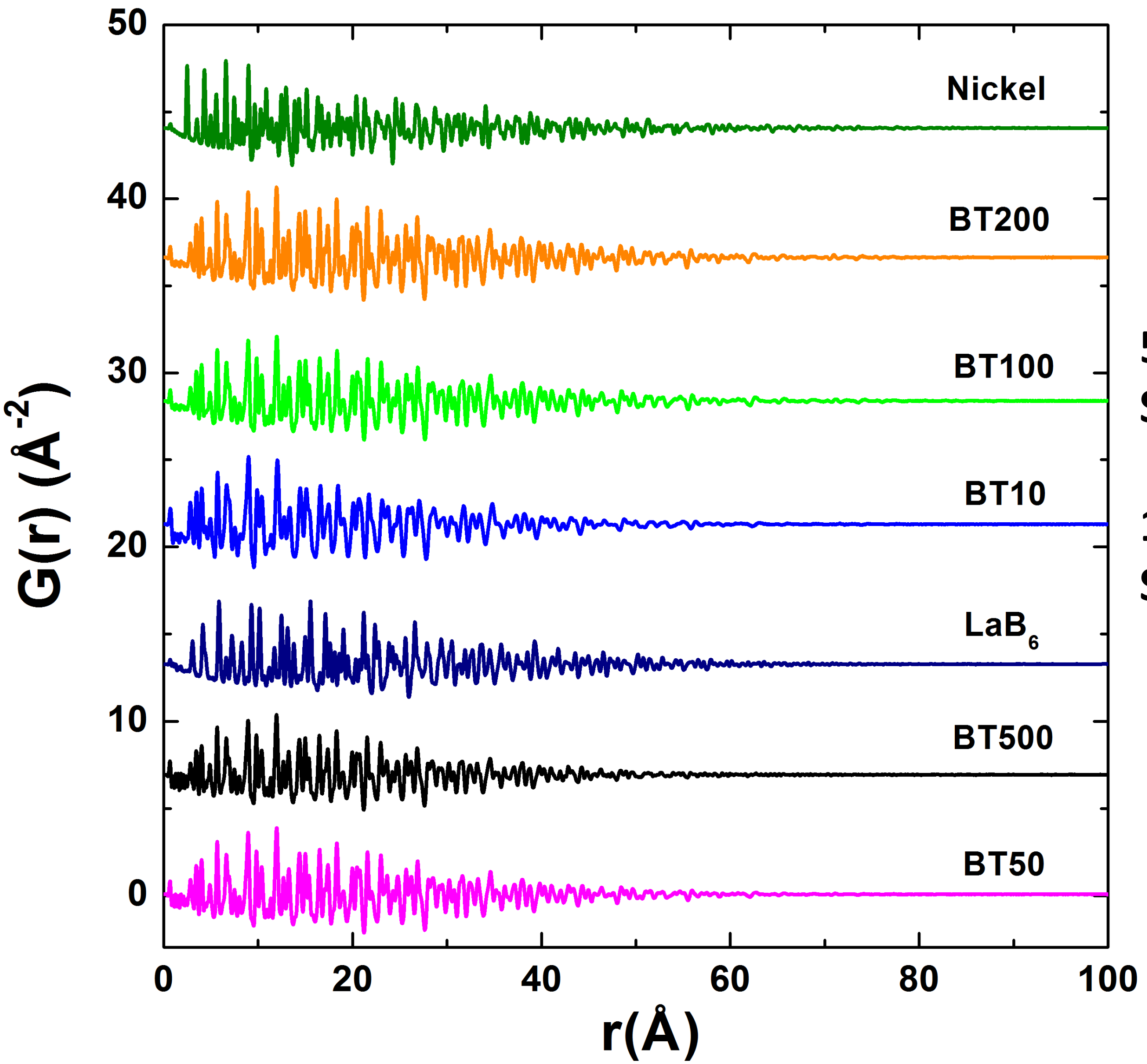
Extra Slides

Preview of results

- **ALL particle sizes show ~ 0.1 Å Ti displacements at ALL temps: 20° to 200°C !**
- **Large (> 200 nm) BTO NPs (bulk) exhibit a sharp structural transition at 120°C**
- **Small (< 200 nm) BTO NPs exhibit instead a gradual crossover with increasing temp.**



aPDFs at Room Temperature (BNL NSLS)



50 nm thru 500 nm from: Sakai Chemical Industries Co.

10 nm synthesized by: Sandia National Labs

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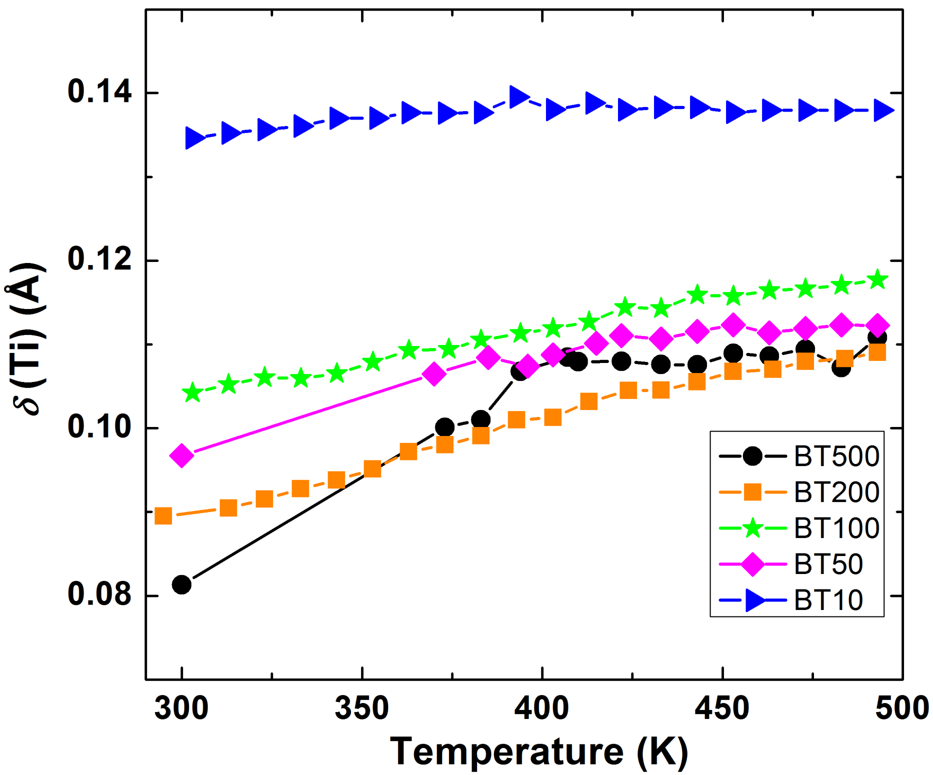
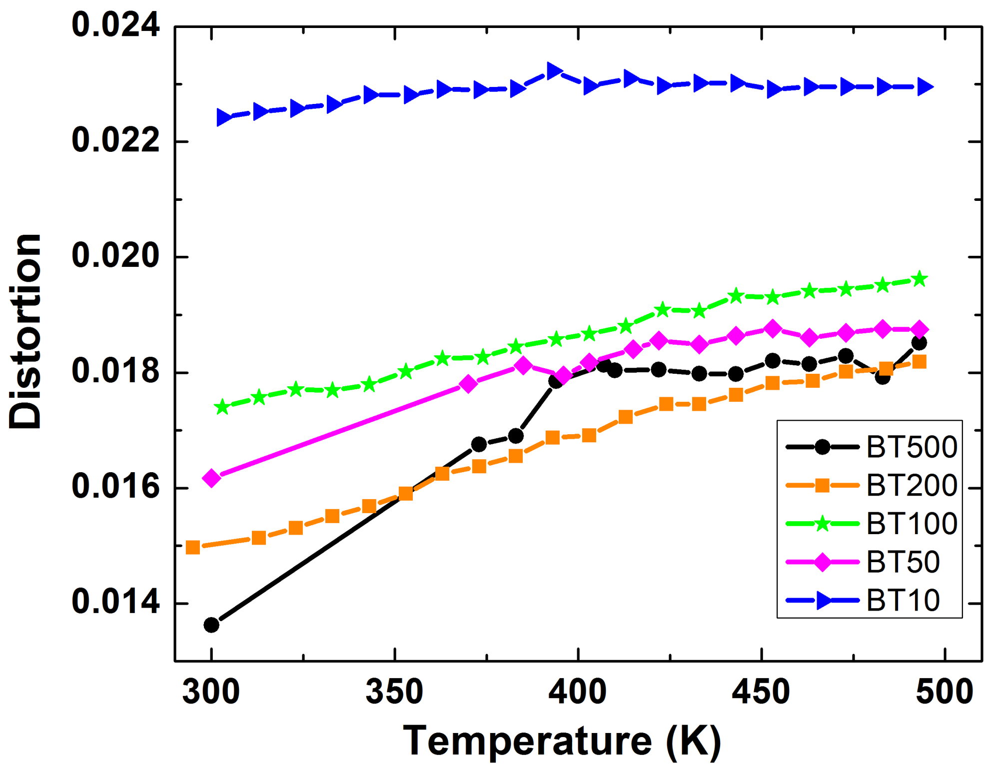
Two Ti displacement Metrics

$Ti_{\delta z}$

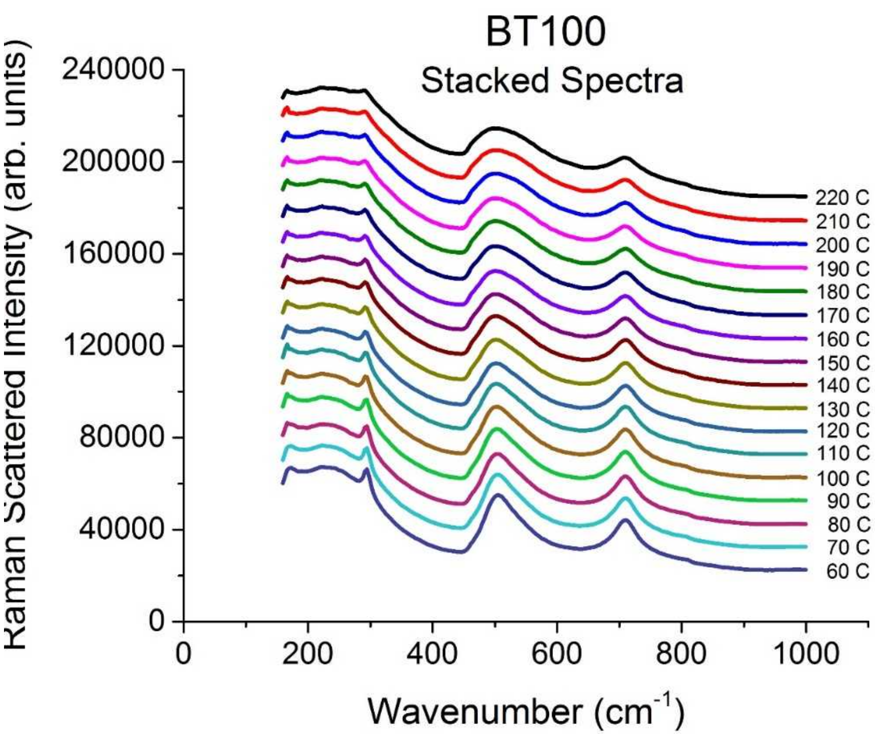
$$\text{Distortion} \equiv \frac{(\text{Ba-Ti})_{long} - (\text{Ba-Ti})_{short}}{(\text{Ba-Ti})_{long} + (\text{Ba-Ti})_{short}}$$

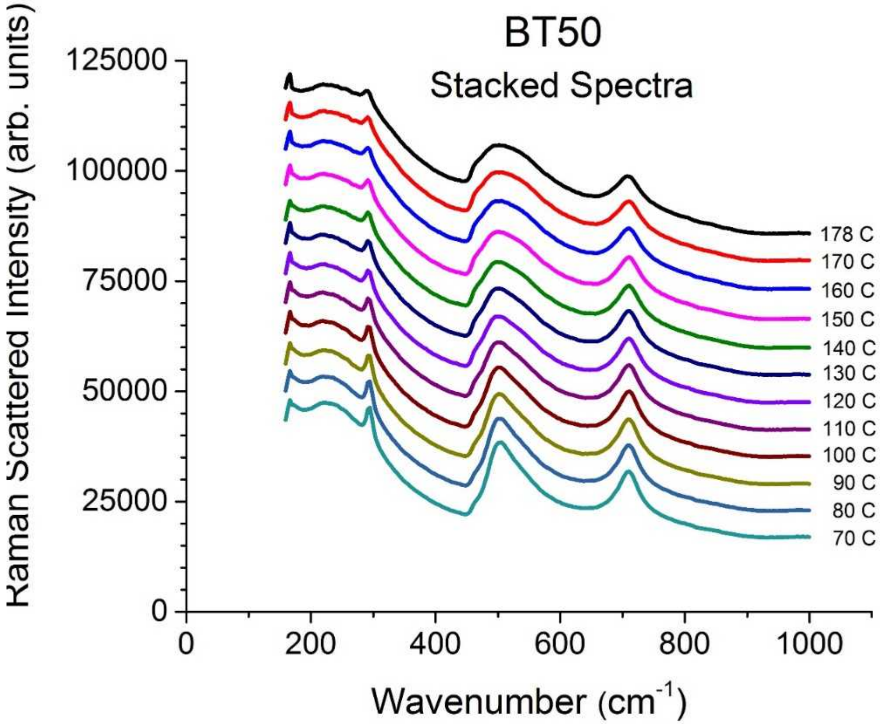




100 nm & 50 nm Raman Comparison

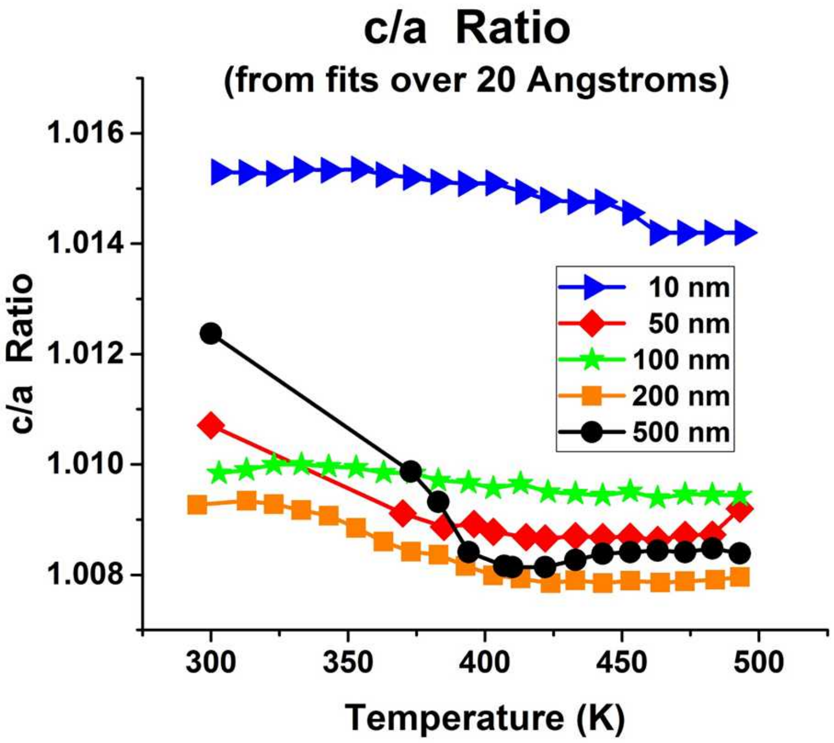
Tetragonal Raman lines for 50 nm BTO NPs persist more strongly above 120°C !



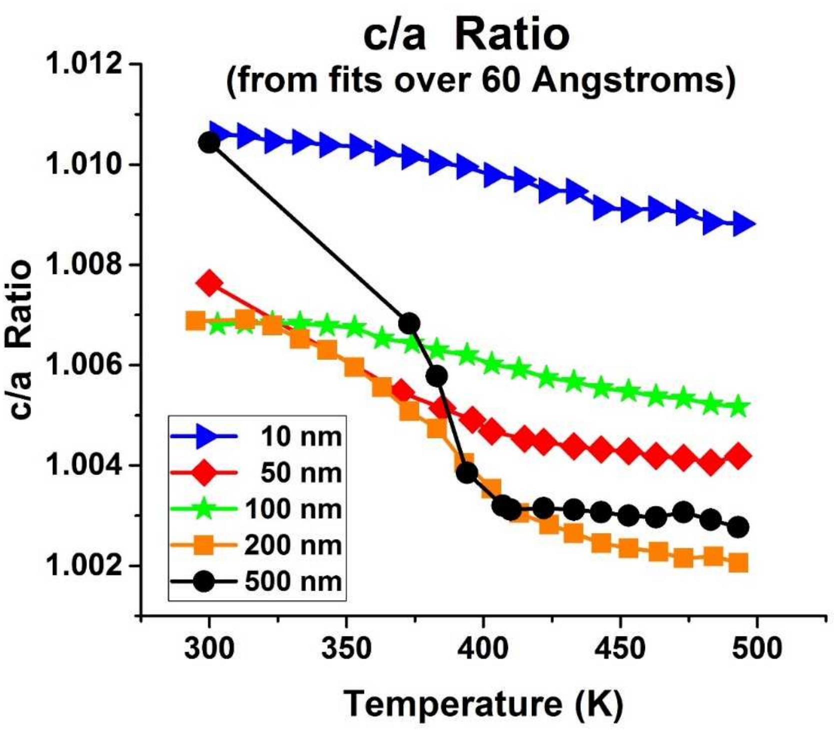


Fit PDFs over a longer range to capture long-range structure!

Fits of PDFs over 20 Å



Fits of PDFs over 60 Å



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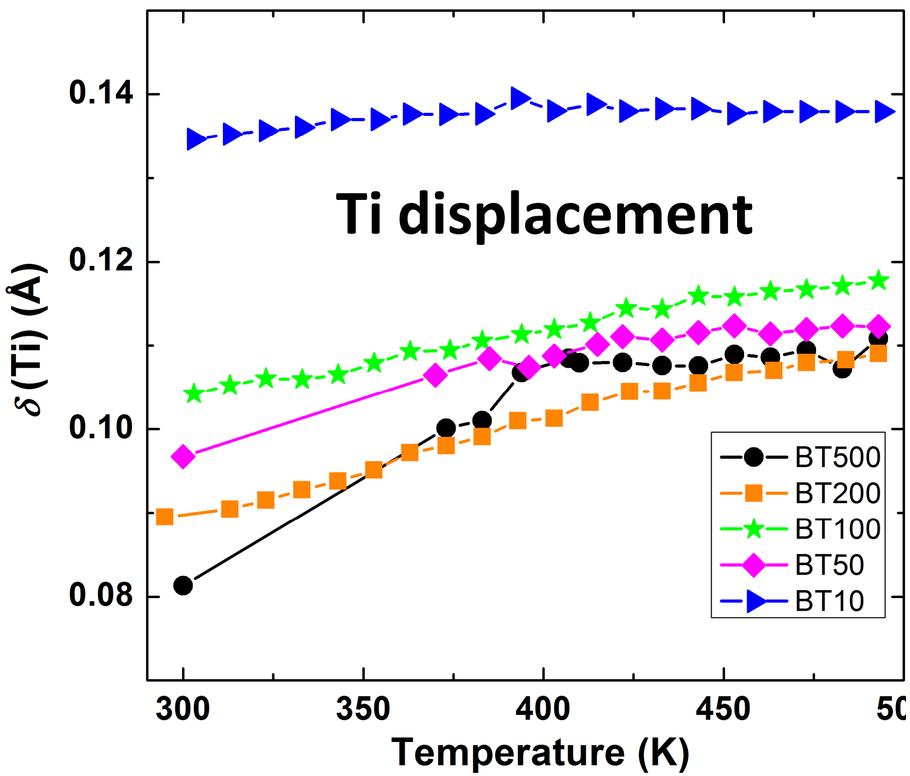
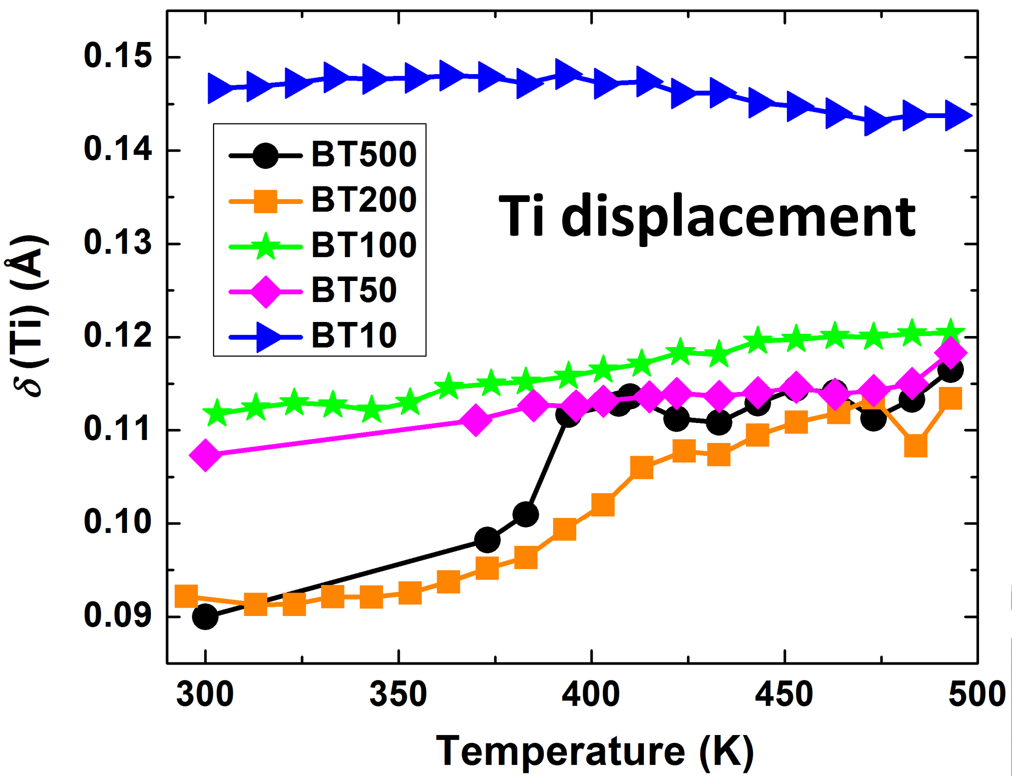
Check Ti displacements over long-range spatial scale!

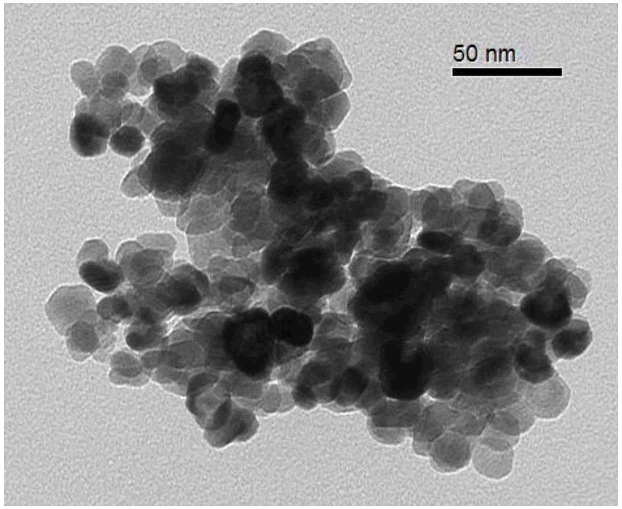
Fits of PDFs over 20 Å

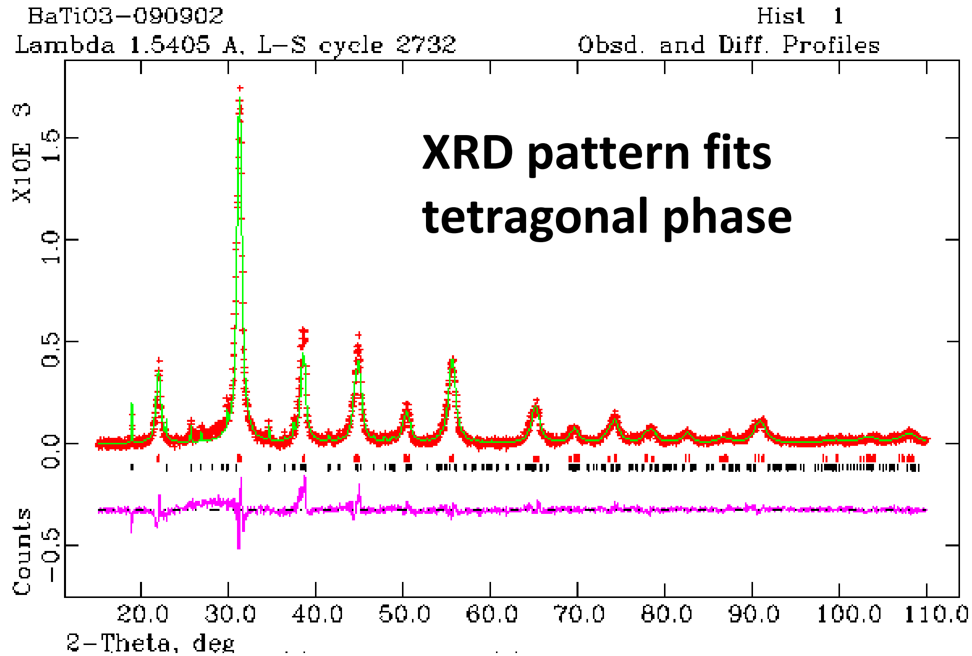


Fits of PDFs over 60 Å



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





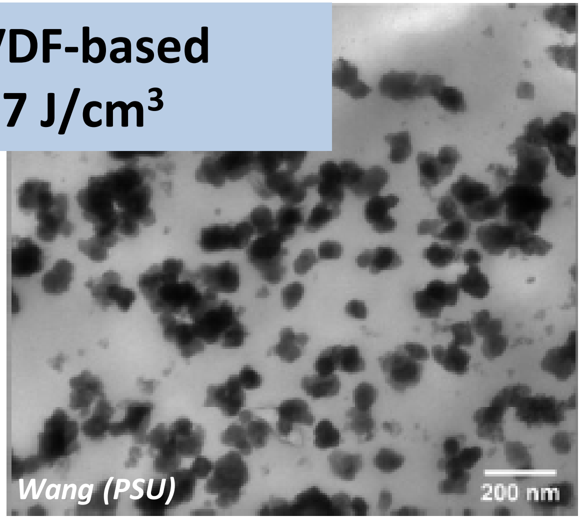
~ 10 nm diameter

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

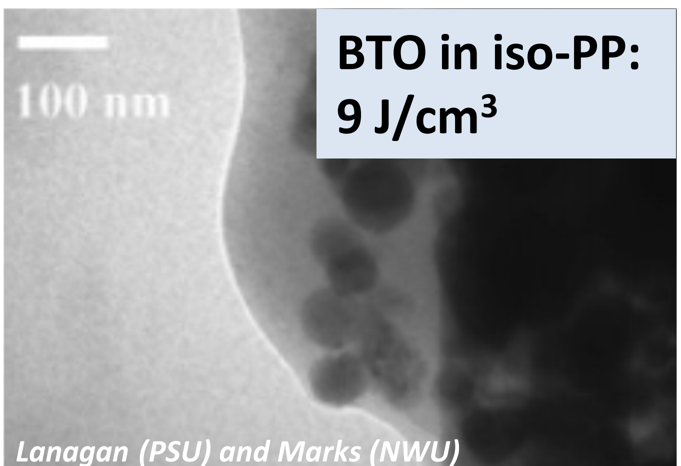
Yoon et. al., *J. Am. Ceram. Soc.* 90 311 (2007)

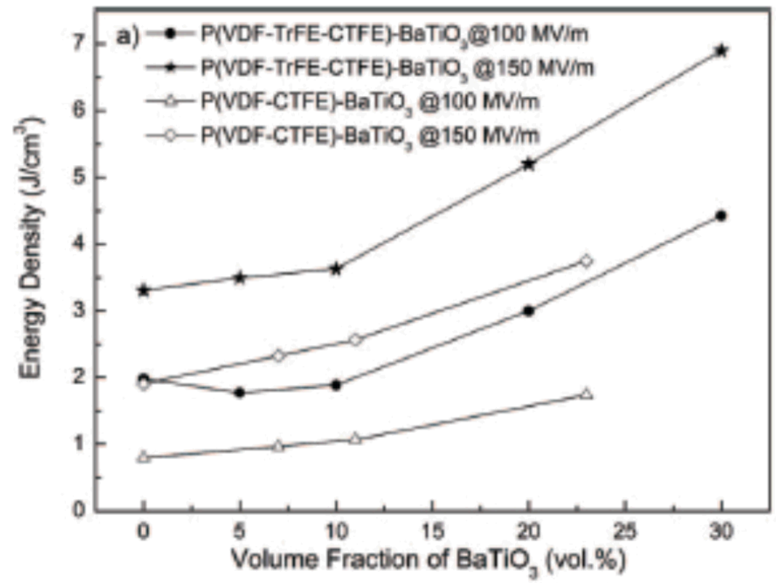
Ceramic/Polymer Nanocomposites

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**

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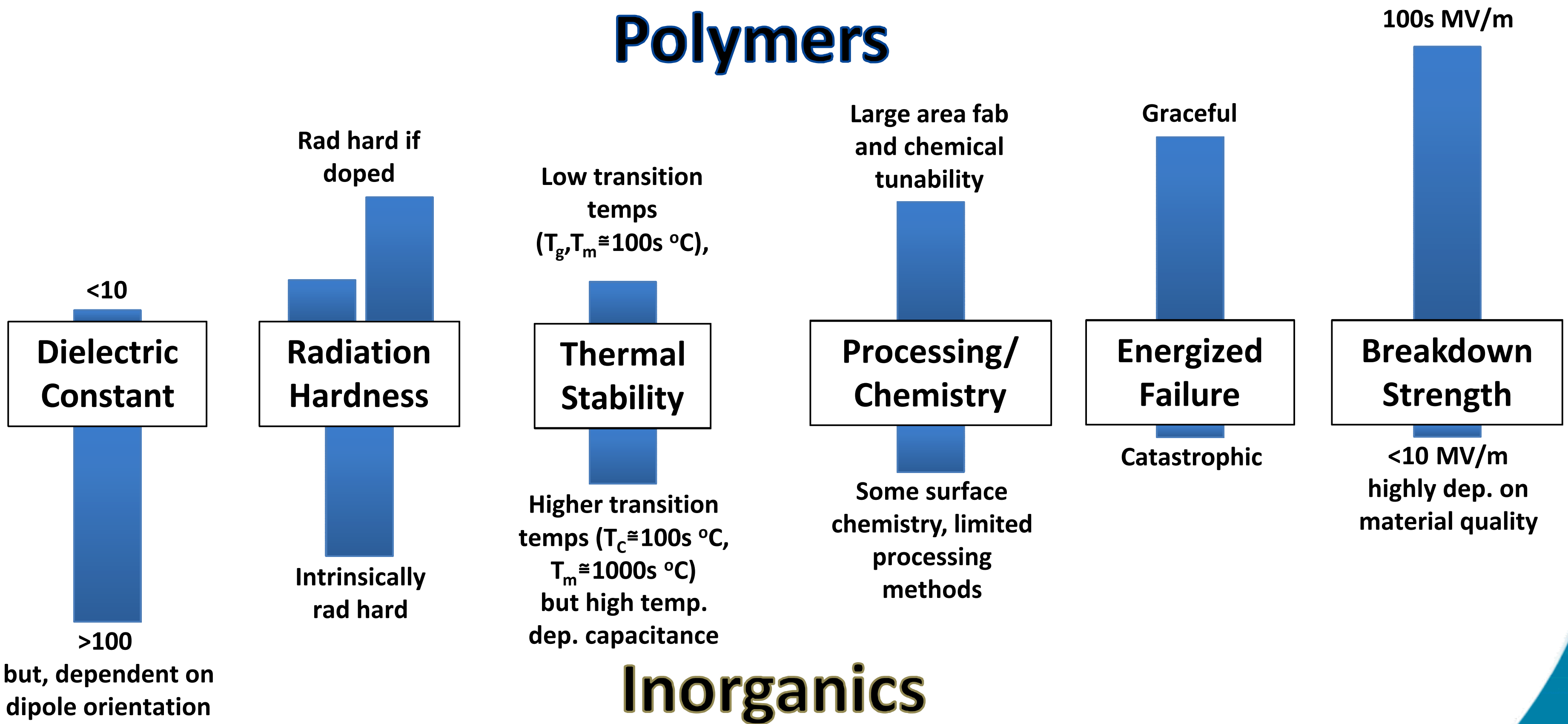
Nanoparticle/Polymer Composite Capacitors

Polymers (e.g., mylar, teflon, etc.) and inorganic ferroelectrics (e.g., $BaTiO_3$, PZT, etc.) have complimentary strengths and weaknesses.



Composites combine the best of both worlds, but must mitigate against worst of both worlds.