SAND2013-4444C

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Optimization of Field Assisted Sintering Technique in Fabrication of Nanostructured $BaTiO_3$

PACRIM 10

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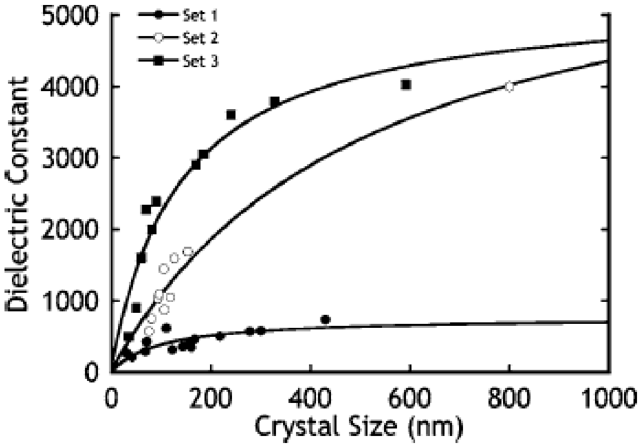
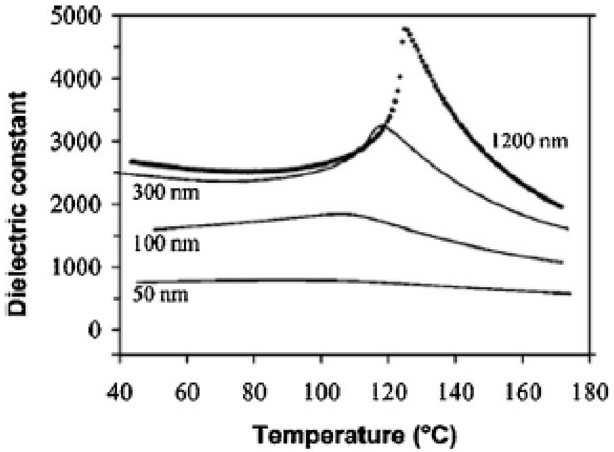
Dense, Sintered, and Nanocrystalline $BaTiO_3$

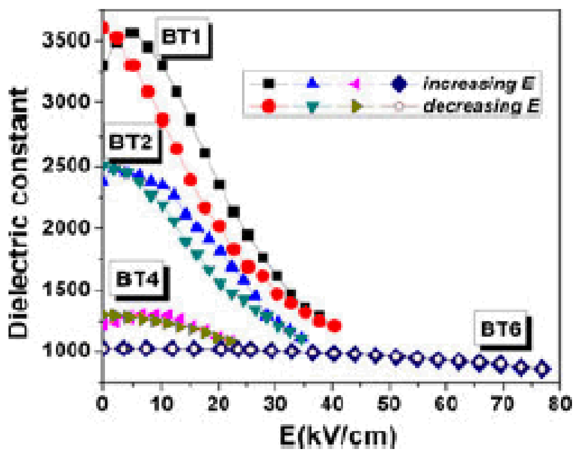


Aygün et. al., J. Appl. Phys. Vol. 109 (2011) 034108

Achieved using FAST:



Zhao et. al., Phys. Rev. B Vol. 70 (2004) 024107
DOI: 10.1103/PhysRevB.70.024107



Curecheriu et. al., J. Am. Ceram. Soc. Vol. 95 (2012) 3912
DOI: 10.1111/j.1551-2916.2012.05409.x

- **Increases in permittivity reported in colloidal $BaTiO_3$ less than ~ 1 μm elusive or impossible to achieve due to grain boundary effects**
- **Uniform control over grain size still allows additional tuning of properties difficult to demonstrate via conventional sintering**
  - **Field dependence of permittivity (VCC)**
  - **Temperature dependence of permittivity (TCC)**

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More Benefits of Nanocrystalline Ferroelectrics

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

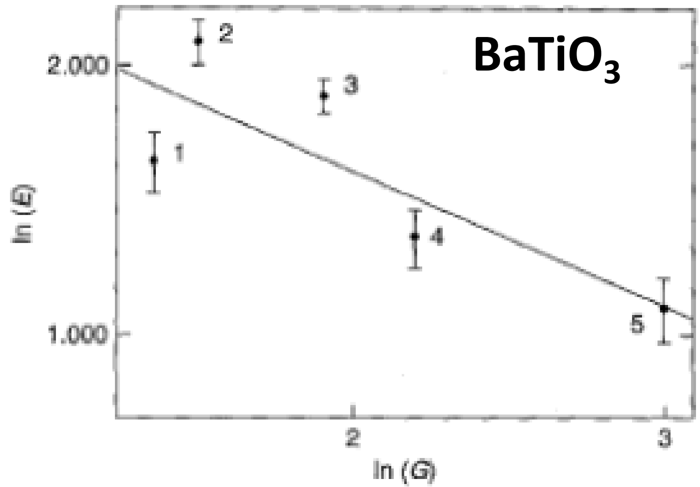


Figure 2 Grain size dependence on dielectric strength. Numbers indicate sintering temperatures: (1) 1320 °C, (2) 1330 °C, (3) 1350 °C, (4) 1380 °C, (5) 1400 °C.

Tunkasiri , et. al., J. Mater. Sci. Lett. Vol. 15 (1996) 1767-1769

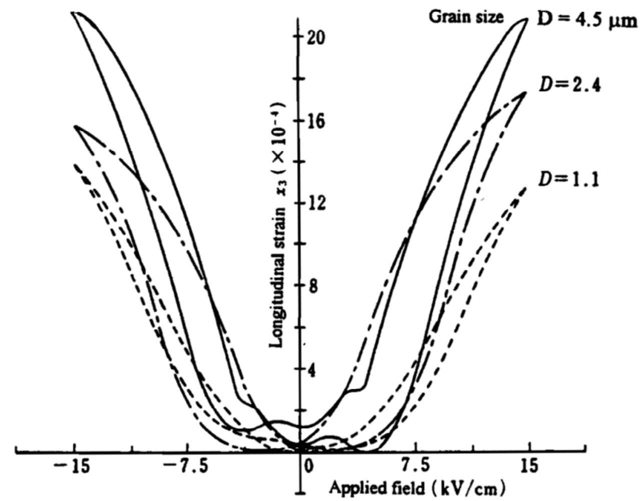


Fig. 3.28 Grain size dependence of the induced strain in PLZT ceramics.

from Kenji Uchino's book, Ferroelectric Devices

Motivation for FAST of $BaTiO_3$

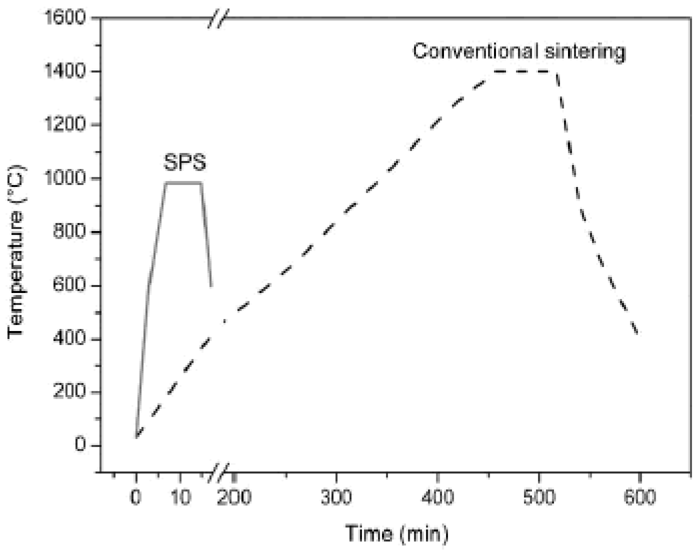


Fig. 4. Comparison of sintering profiles of $BaTiO_3$ ceramics obtained by conventional sintering and by SPS.[10]

Hungría et. al., Adv. Eng. Mater. Vol. 11 (2009) 616
DOI: 10.1002/adem.200900052

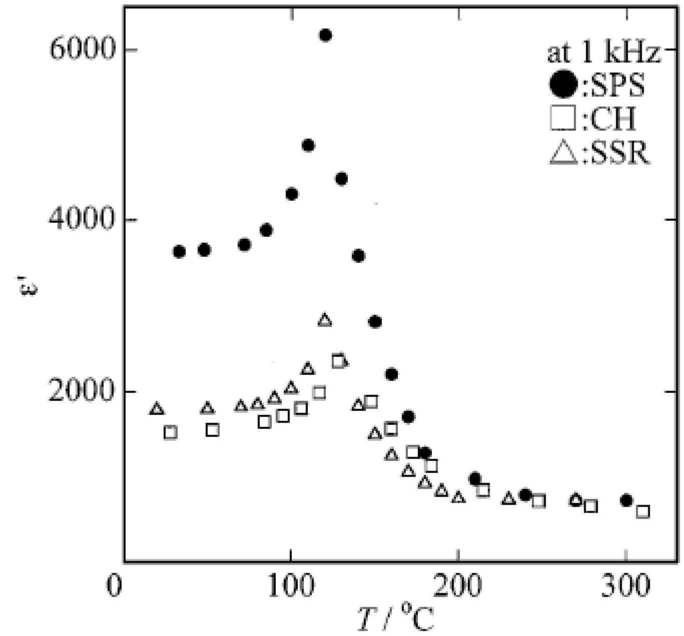


Figure 5 Temperature dependence of the permittivity at 1 kHz for SPS, CH and SSR $BaTiO_3$ pellets.

Takeuchi et. al., J. Mater. Sci. Vol. 34 (1999) 917

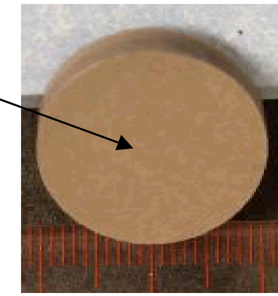
- **Dramatically shorter sintering times**
- **Lower sintering temperatures**
- **Ability to limit/control grain sizes**
  - **Porosity and oxygen defects minimized at same time**
- **Effective in removing resistive grain boundary component commonly observed in conventionally sintered BTO**
- **Improved frequency response**

Field Assisted Sintering Technique (FAST)

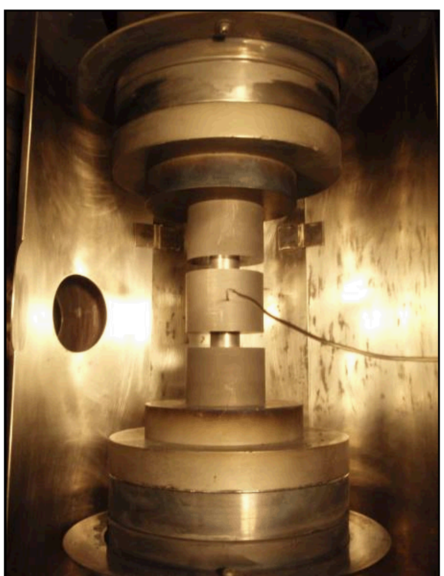
SPS Model: SPS-825S Dr. Sinter® at UCD

Starting Powder in Die

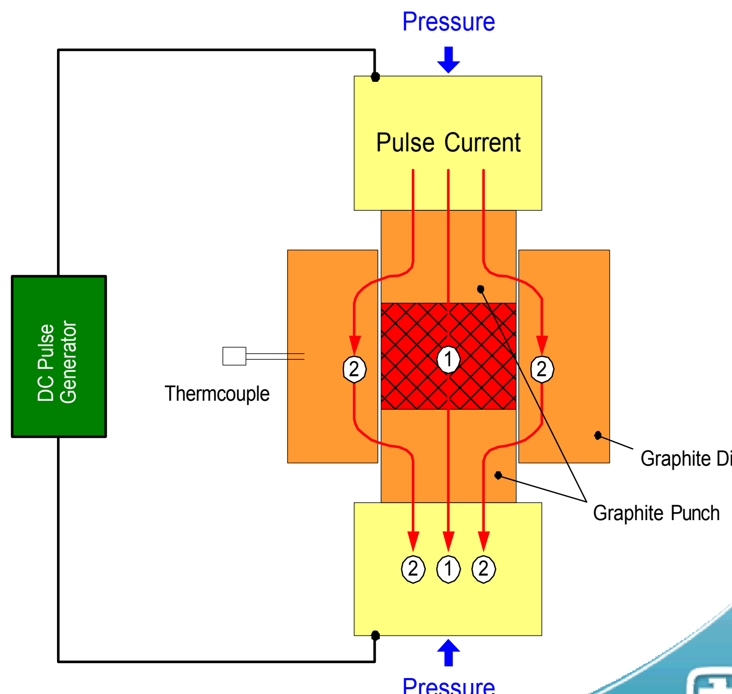
End Product



SPS Synthesis Chamber

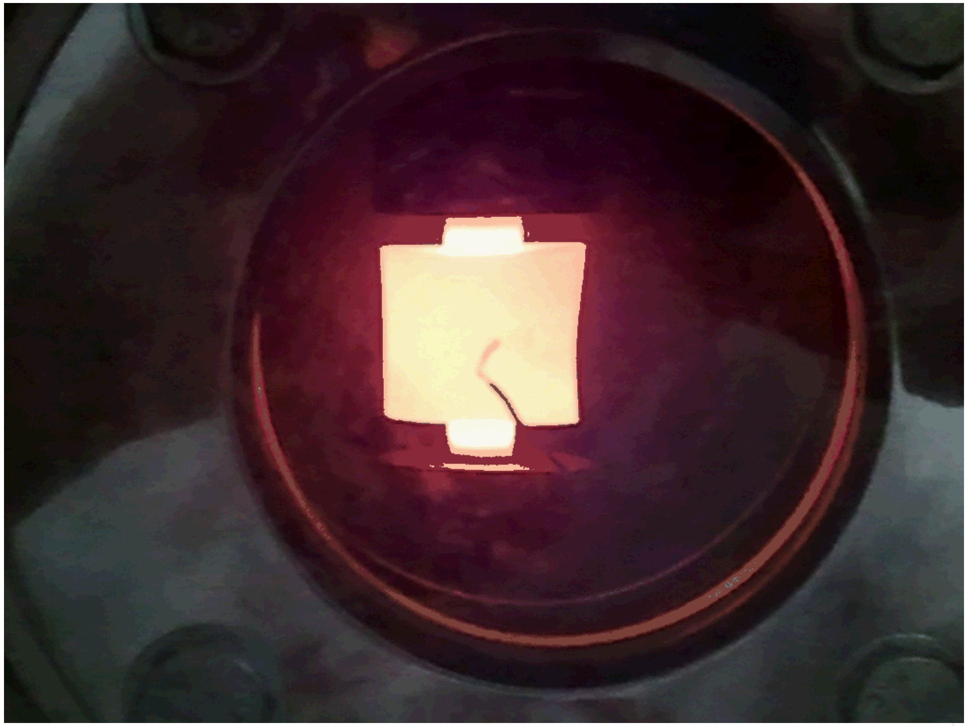


Schematic



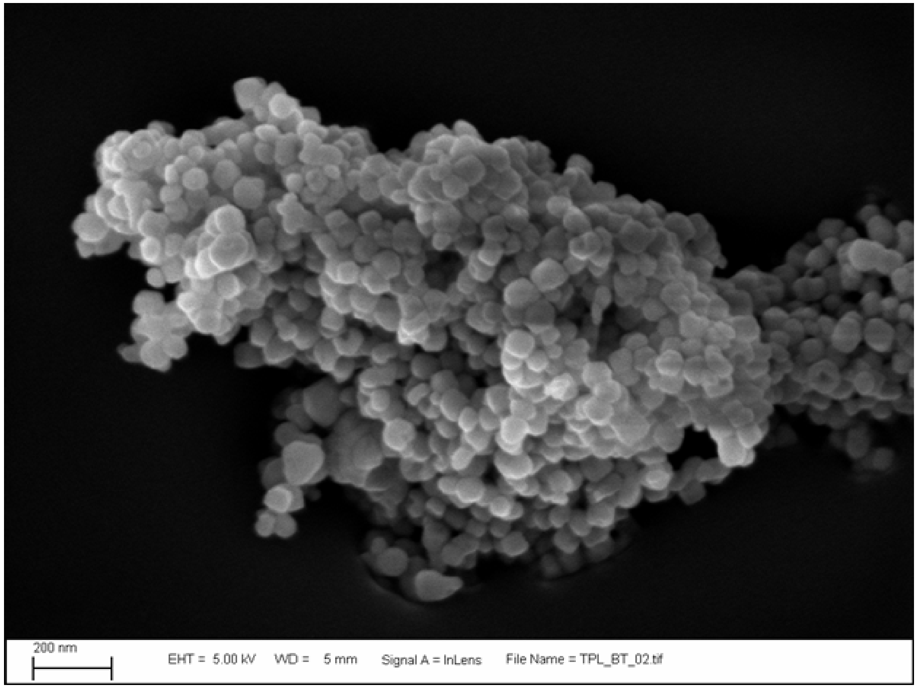
Field Assisted Sintering Technique (FAST)

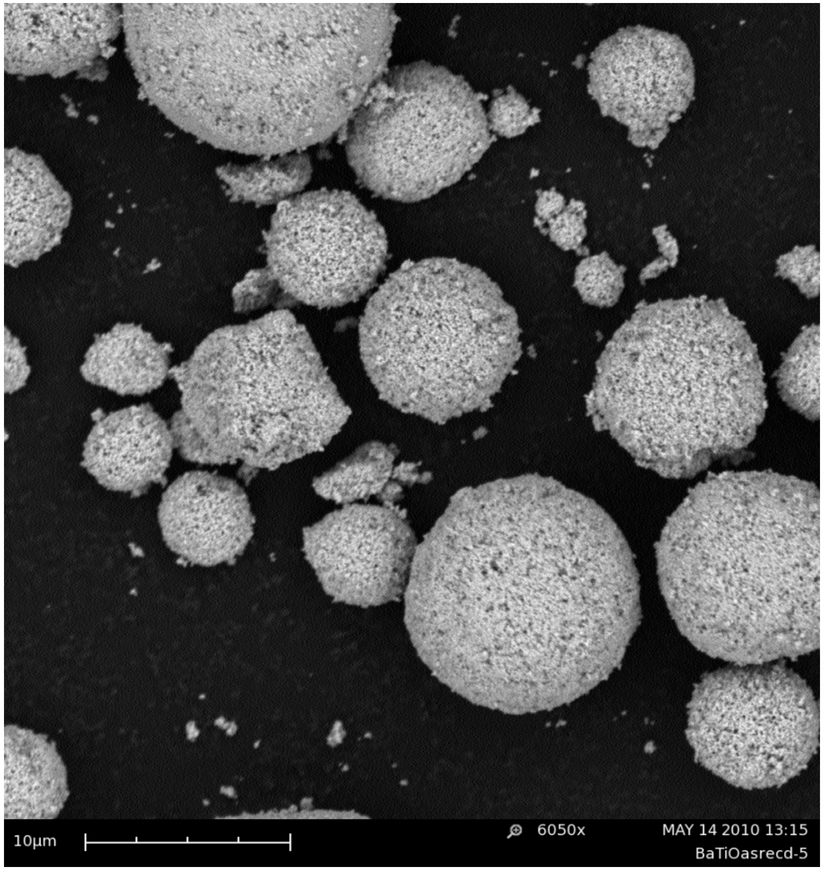
- DC current
  - ON(1-99 ms)/OFF(1-9 ms) pulse
- Surface activation
  - Electromigration
- Short time
  - 5~30 min
  - Max. heating rate ~ 400 ˚C/min
- SPS-825S
  - Max. force: 250 kN
  - Max. current: 8000 A
  - Sample dimension: Φ80 mm



- Offers the ability to fine tune grain size in sintered devices

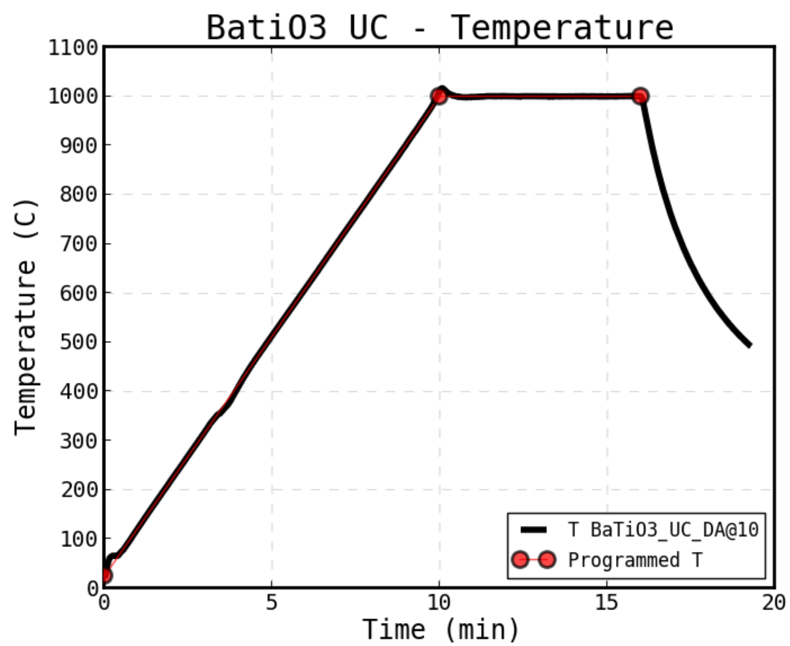
$BaTiO_3$ from TPL

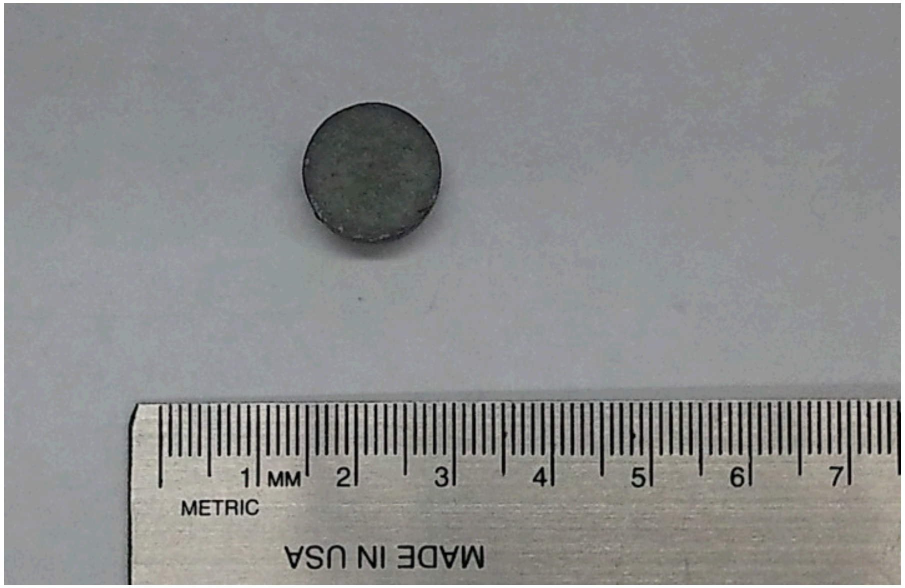




- **NanOxide HPB-1000 from TPL**
- **BET surface area of 16.26 ± 0.0669 m^2/g**
- **60-80 nm primary particle size**
- **1-20 µm "soft" agglomerates**

Initial Sintering Parameters





- Used TPL powders calcined at 500°C
- Heat to 1000°C in 10 min
  - Hold at 1000°C for 6 min
- Apply 90 MPa at 350°C
- No changes in SPS vacuum detected (no outgassing)

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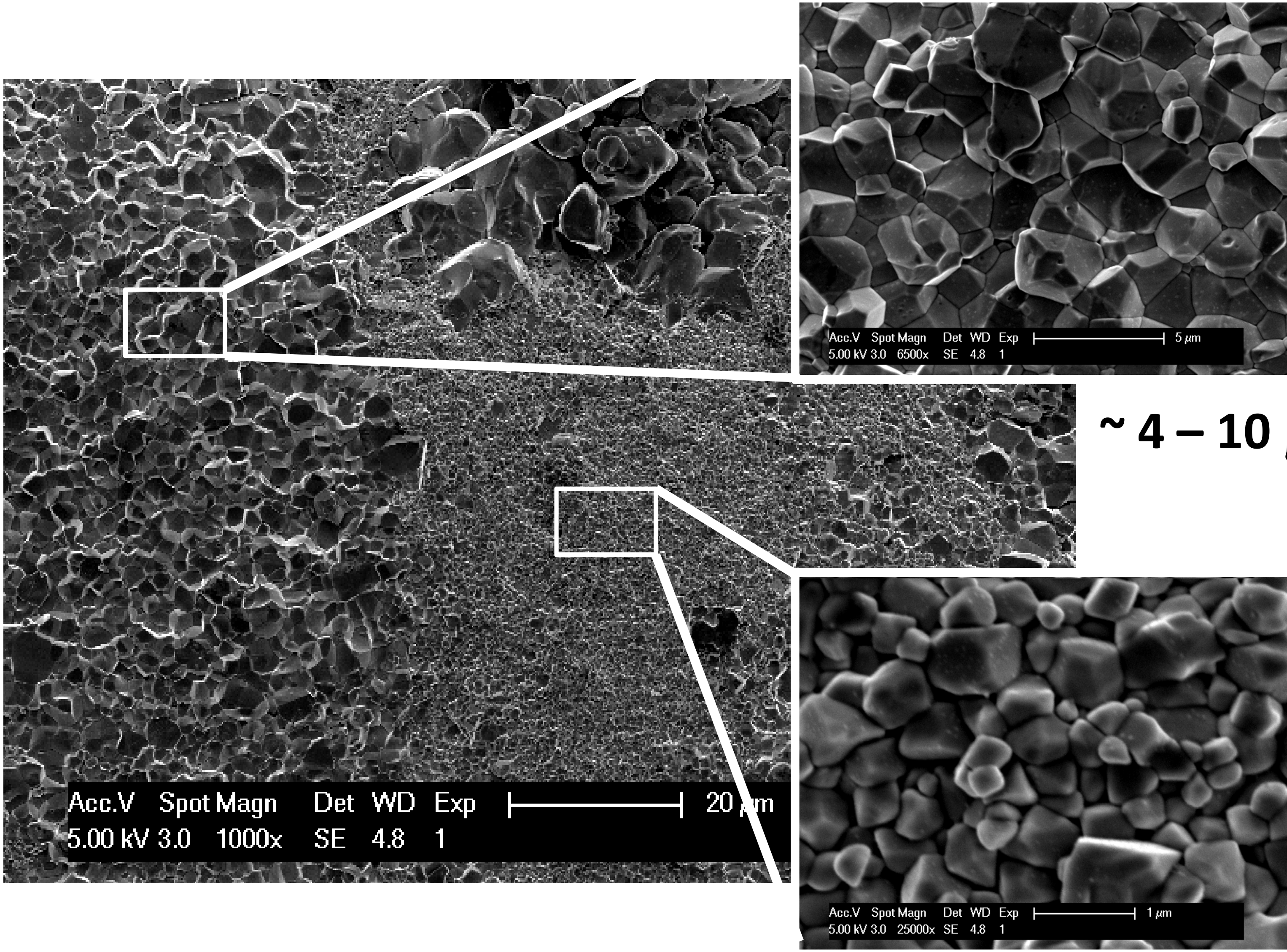
Abnormal Grain Growth, 1000 °C, 6 min. hold

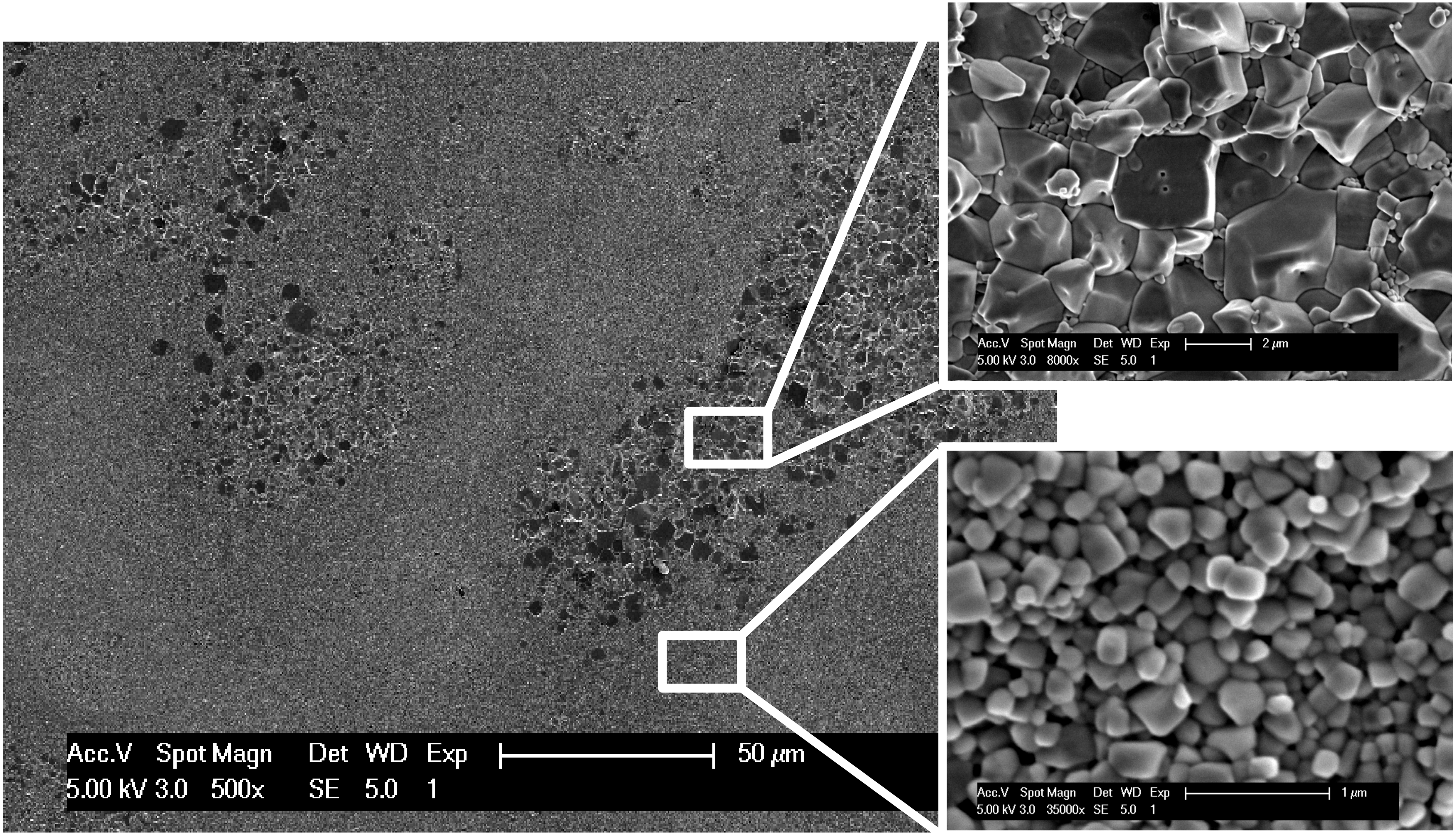


~ 4 – 10 μm

~ 500 nm

Abnormal Grain Growth, 950°C, 3 min. hold

~ 3 μm

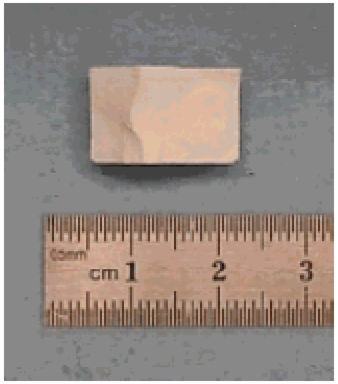


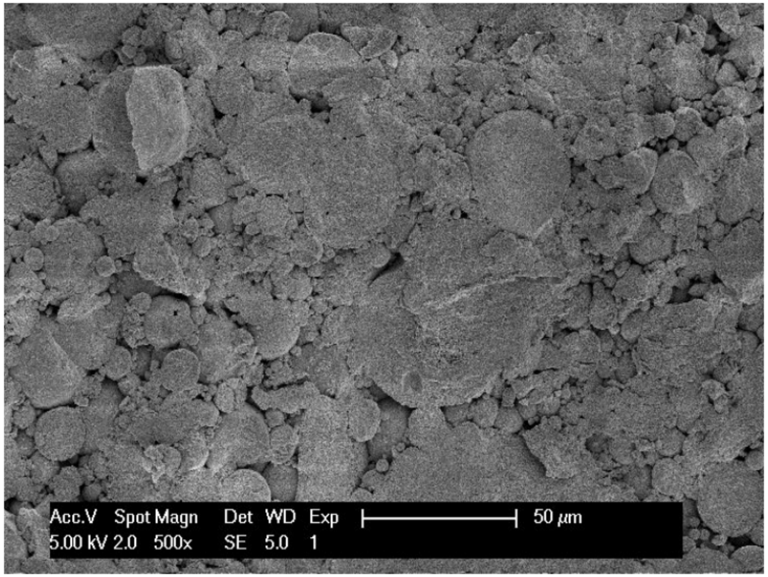
~ 200 nm

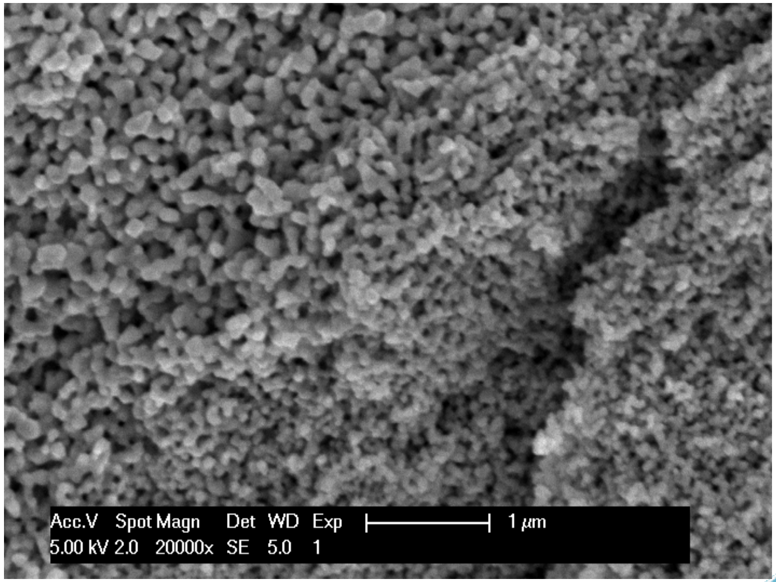
Possible to lower sintering temperature further

“Pressureless” Sintering Experiments

- Apply minimal pressure during sintering (P<20MPa)
- White color remains
- Chalky, brittle
- Minimal consolidation
- No nanoparticle growth







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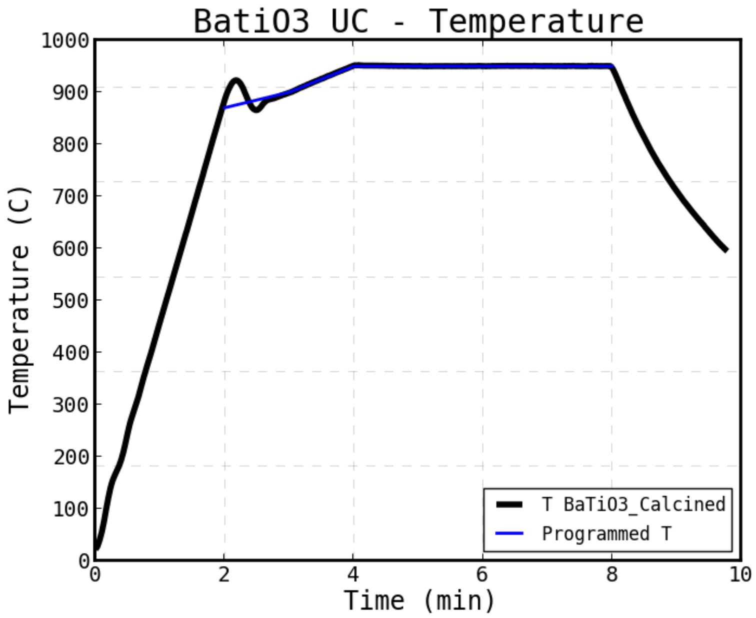
Fast Heating Rate Experiments

Achieving earlier onset of volume diffusion would minimize grain growth and possibly aid in preventing AGG

Profile:

- **RT → 870°C for 2min**
  - **435°C/min**
- **870°C → 950°C for 2min**
- **Hold 950°C for 2min**
- **90MPa applied at RT**



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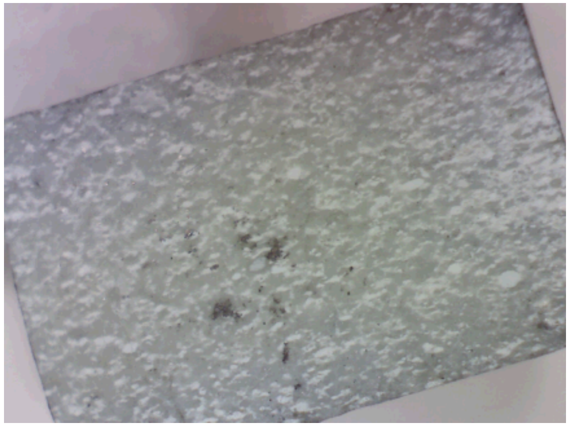
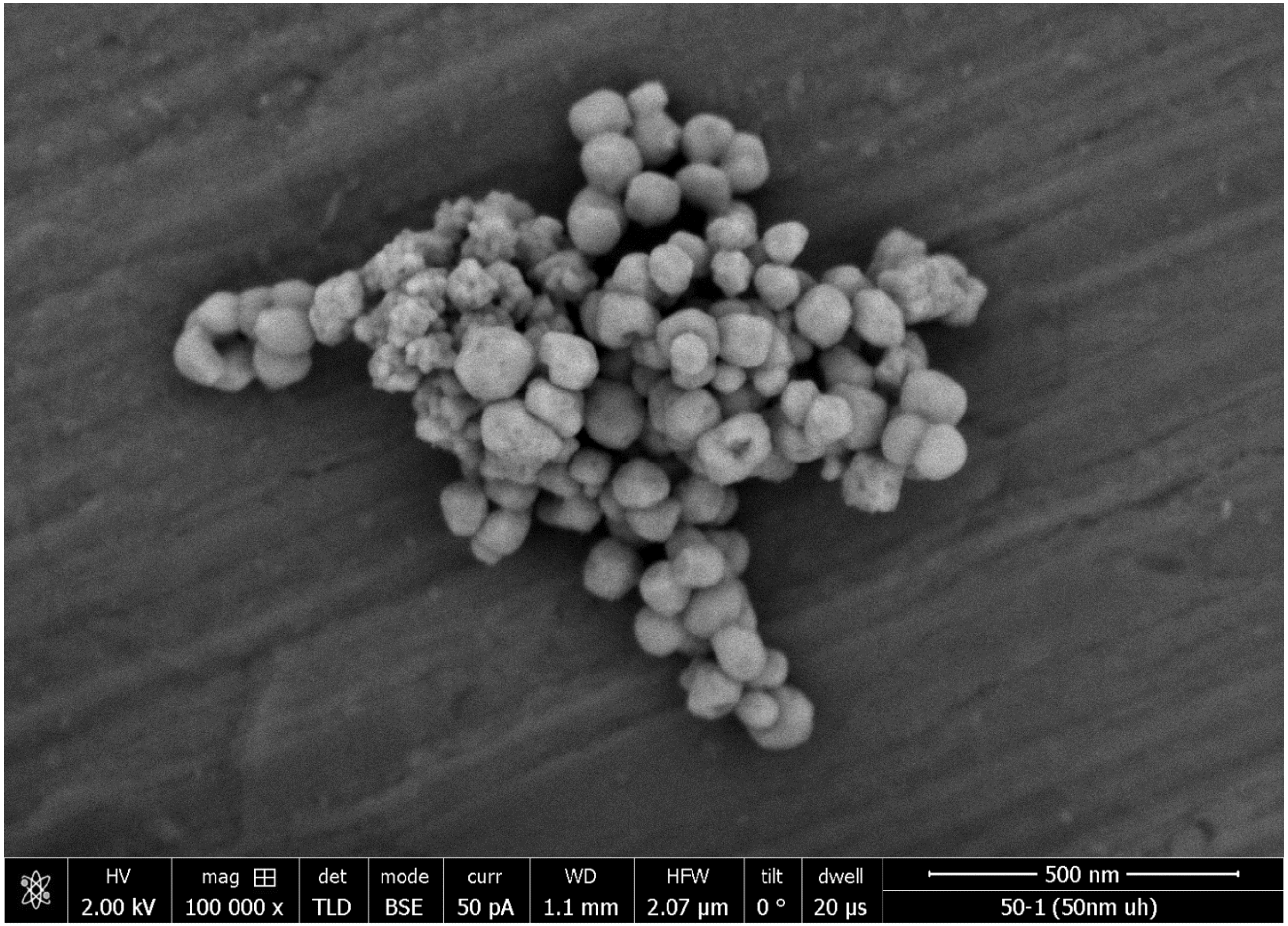
Fast Heating Rate Experiments

- **Full densification achieved at holding times ranging from 2-6 minutes**
- **AGG still observed in all samples**



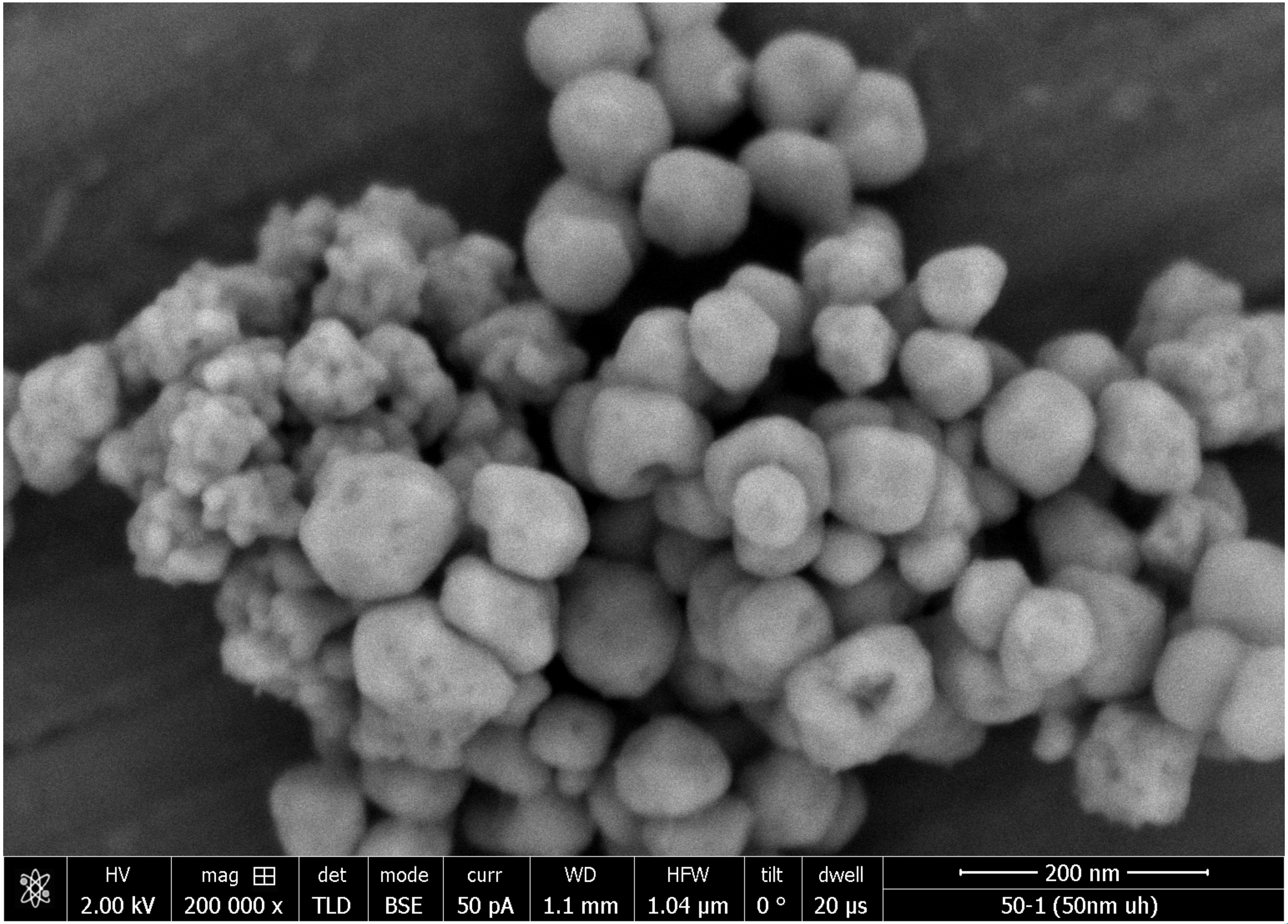
Name	Holding Time min	ρ [vol] g/cm^3	ρ% [vol]	ρ [arch] g/cm^3	ρ% [arch]
1.1.6 [1]	6	5.81	96.6	5.86	97.4
1.1.7 [1]	5	5.85	96.8	5.82	96.9
1.1.8 [1]	4	5.61	93.3	5.83	97.0
1.1.9 [1]	3	5.73	95.3	5.85	97.2
1.1.10 [1]	2	5.44	90.4	5.67	94.2

SEM image of TPL BTO



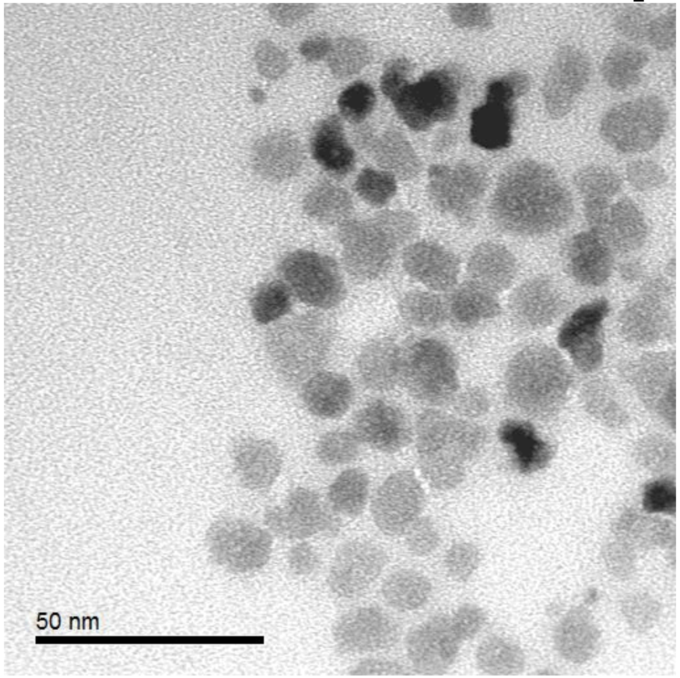
- **Large dispersion in primary particle size**
- **In addition to agglomeration, size dispersion may be contributing to AGG**

SEM image of TPL BTO

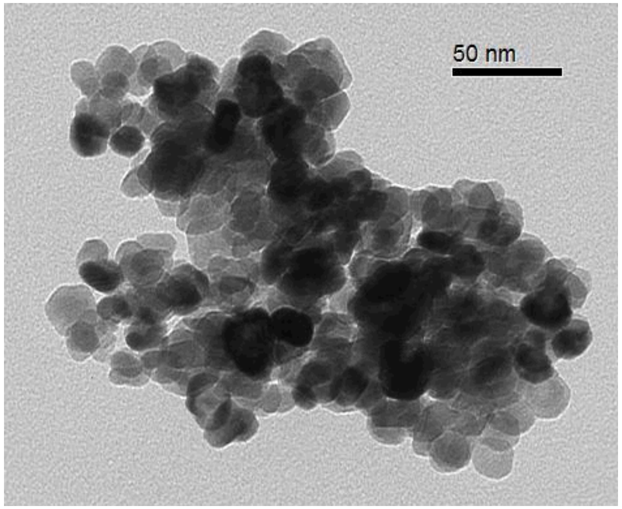


AGG Mitigation Strategies

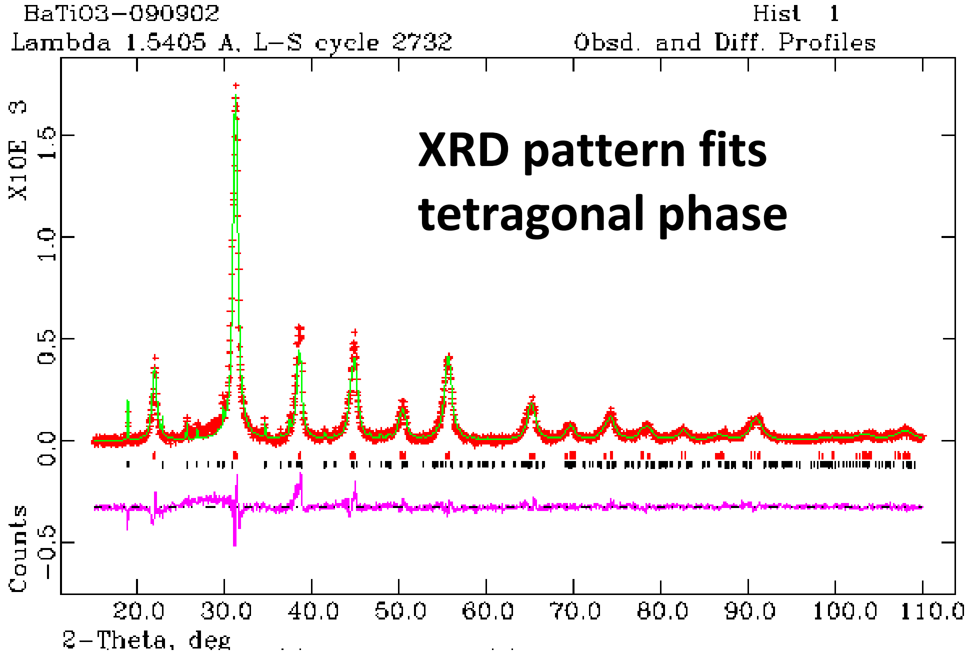
- **Increase applied pressure during FAST**
  - **Ensure applied stresses are more uniform**
- **Decrease FAST temperature**
- **Deagglomerate starting powder**
  - **Sonication, milling, homogenization**
- **Start with more uniform and dispersed particles**



$BaTiO_3$ 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

Provisional Patent Filed: # 61586887

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

Conclusion

- **Good densification of $BaTiO_3$ nanoparticles demonstrated via FAST**
- **AGG evident in sintered pellets**
  - AGG has been eliminated but still exists at a problematic level
- **Plan to reduce/eliminate AGG**
  - Adjust FAST parameters
  - Pre-process starting powders
  - Transition to more uniform and dispersed BaTiO3 synthesized at SNL

Related Poster:

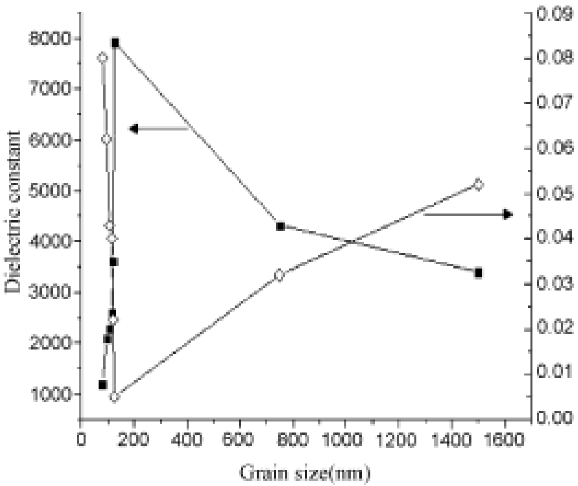
Measuring the Permittivity of Nanoparticle Powder Slurries, Tonight

Acknowledgements: Chris DiAntonio, Pin Yang

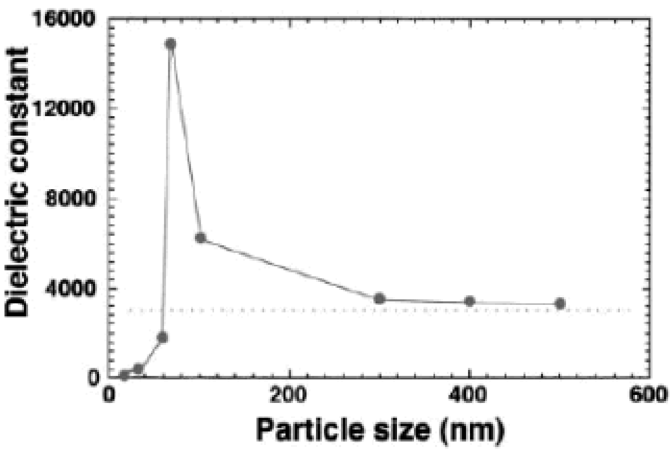
Extra Slides

Benefits of Nanocrystalline Ferroelectrics

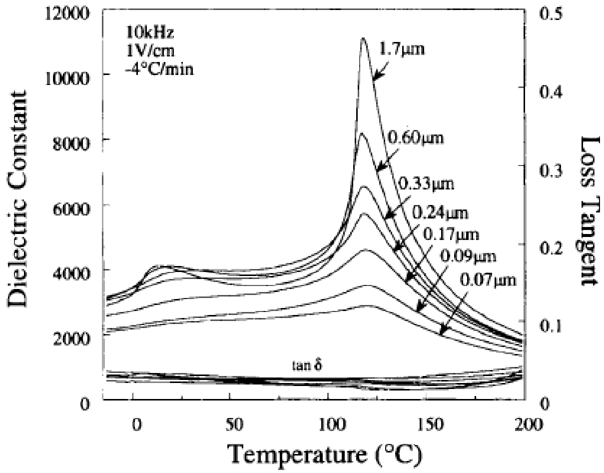
- **Permittivity increases with decreasing grain size down to a critical size dimension (higher energy density)**
- **High frequency performance improves with decreasing grain size (maintain permittivity and low loss to higher frequencies)**
- **Field and temperature dependence of permittivity may improve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



Ying and Hsieh, Materials Science and Engineering B 138 (2007) 241–245

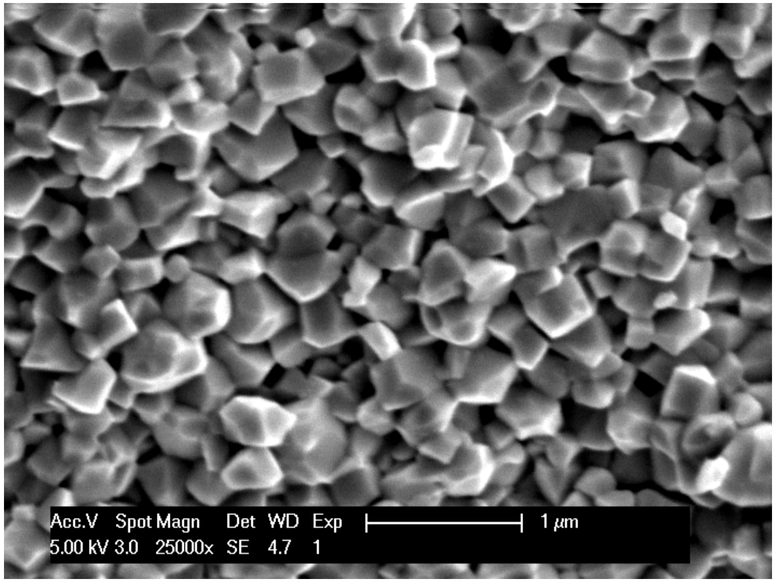


Wada et. al., Jpn. J. Appl. Phys. Vol. 42 (2003) 6188–6195

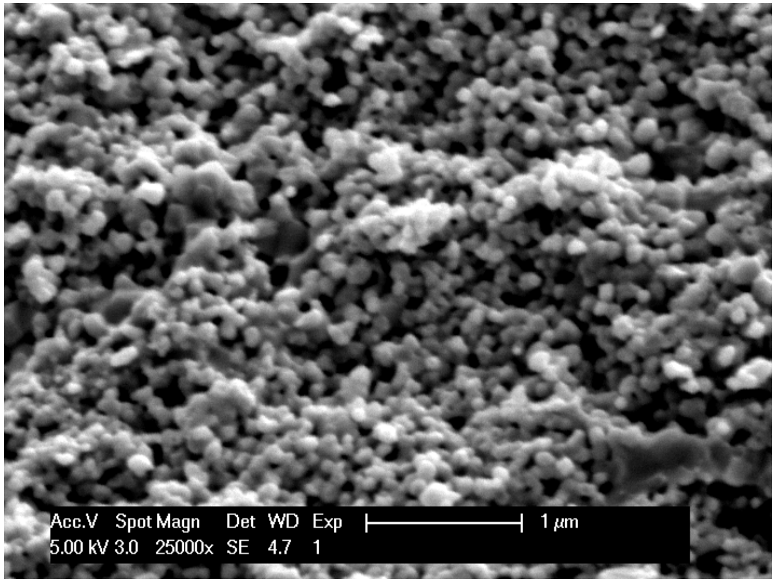


Frey, et. al., Ferroelectrics, Vols. 206-207, (1998) 337-353

SEM of SPS BTO



TPL BTO, grain size 300 – 400 nm



SNL BTO, grain size 100 – 200 nm

- **Spark Plasma Sintering (SPS)**
- **BTO powders pre-calcined**
- **SPS at 950 ˚C**

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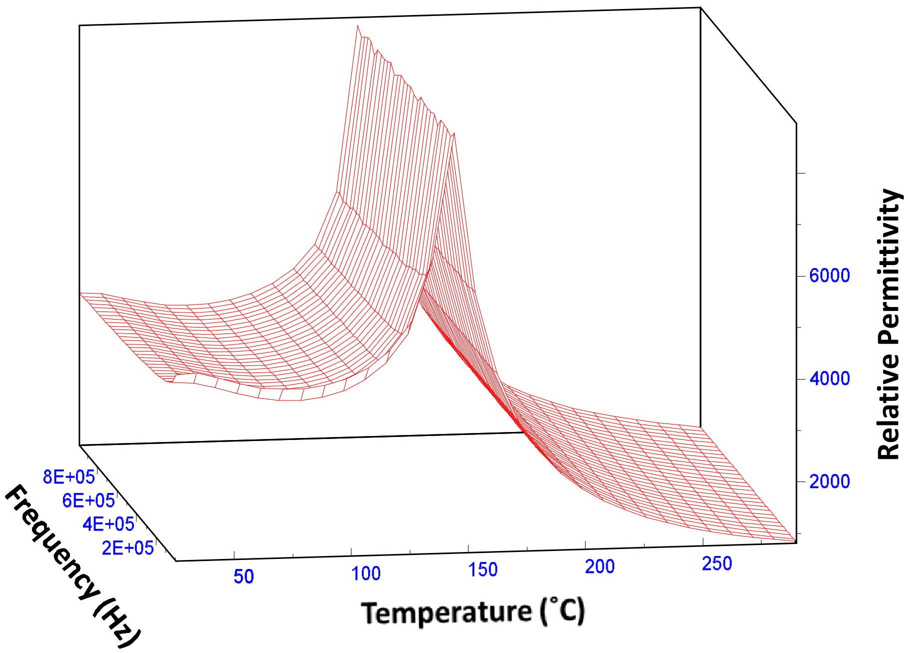
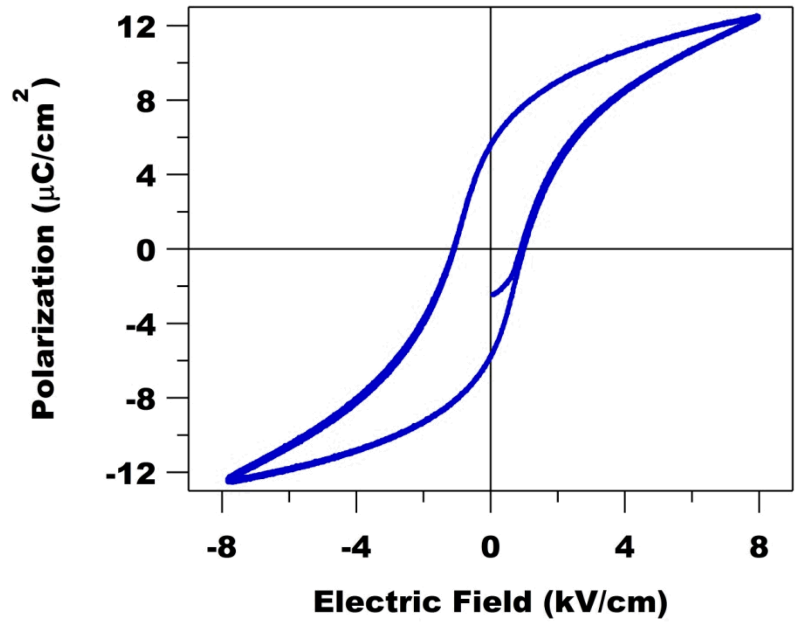
SPS BTO Electrical Results





- TPL BTO Sample
- Weak field permittivity results
- Initial high field results
  - Not taken to electrical breakdown yet

Agglomeration Breakup Study

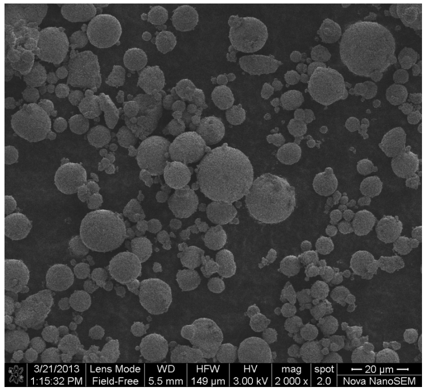
- **Study the influence of agglomerates on final sintered bulk**
- **Procedure**
  1. **Lightly sonicate in ethanol using sonic want (see right)**
     - ***Total on time: 34 min, 2 sec (2 sec on, 7 off)***
     - ***Energy=14092 J, Amplitude=25%***
  2. **Bake at 150°C (2 hrs)- to evaporate ethanol**
  3. **Calcine at 450°C (2 hrs)**
  4. **Re-grind using mortar & pestle (15 min) in Ar glovebox**
  - ***As received (from TPL): No treatment***
  - ***Powder ARC (as received, calcined): Steps 3 and 4***
  - ***Powder SC(sonicated, calcined): Steps 1, 2, 3, and 4***
  - **Field Assisted Sintering Technique(FAST)**
    - ***Heat to 1000°C in 10 min, hold at 1000°C for 6 min in vacuum***
  - **Characterization**
    - ***Density (Archimedes)***
    - ***XRD***
    - ***SEM***

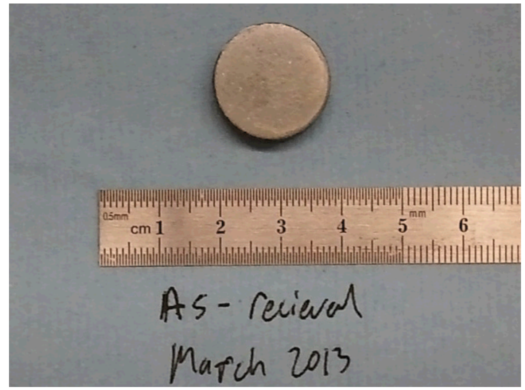
Sonic wand apparatus

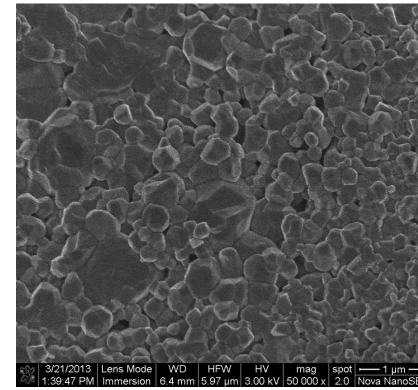
Experimental results: FAST Sintering

SEM image of the feedstock | Digital sintered discs | SEM of sintered disk

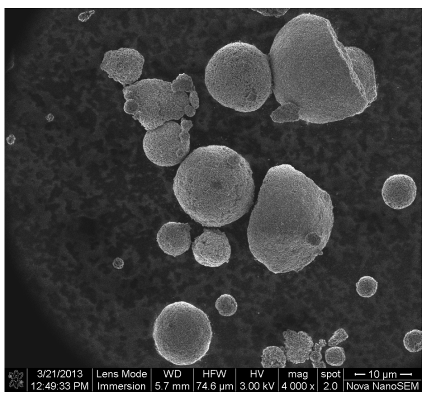
As-received

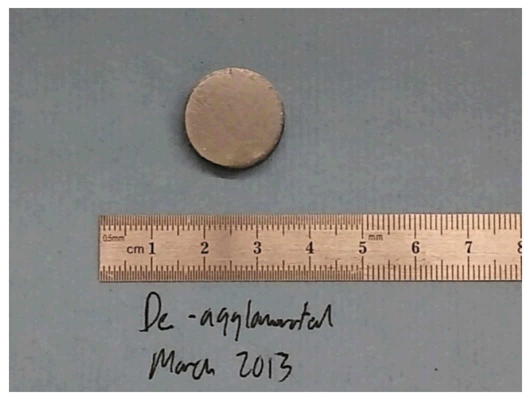


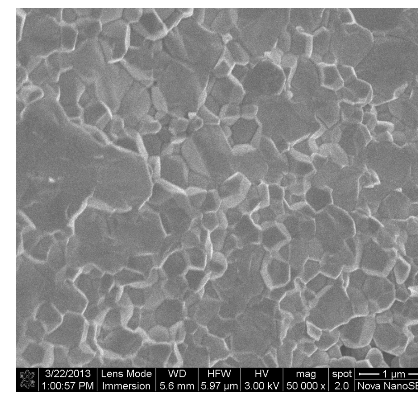




Sonicated

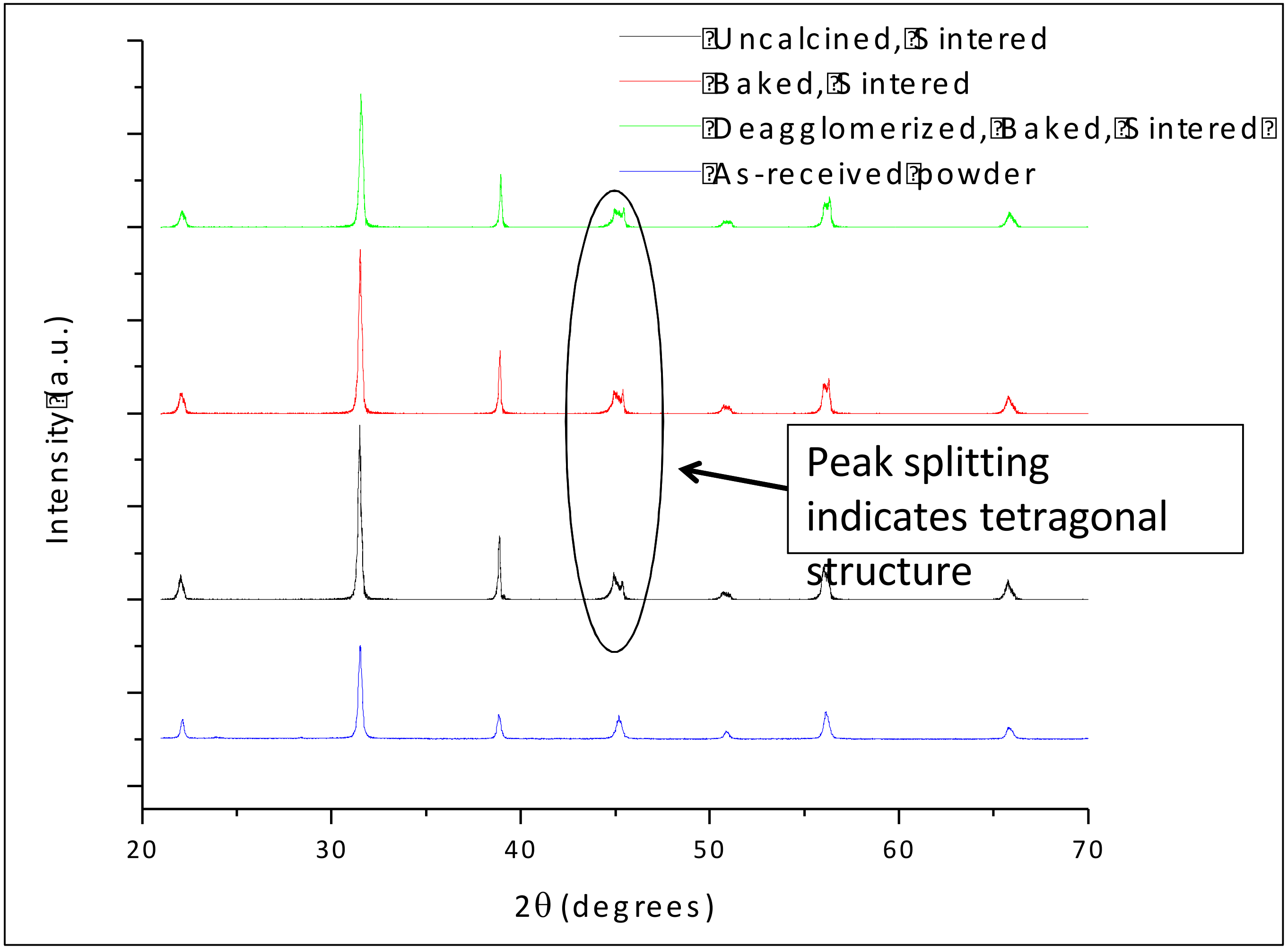






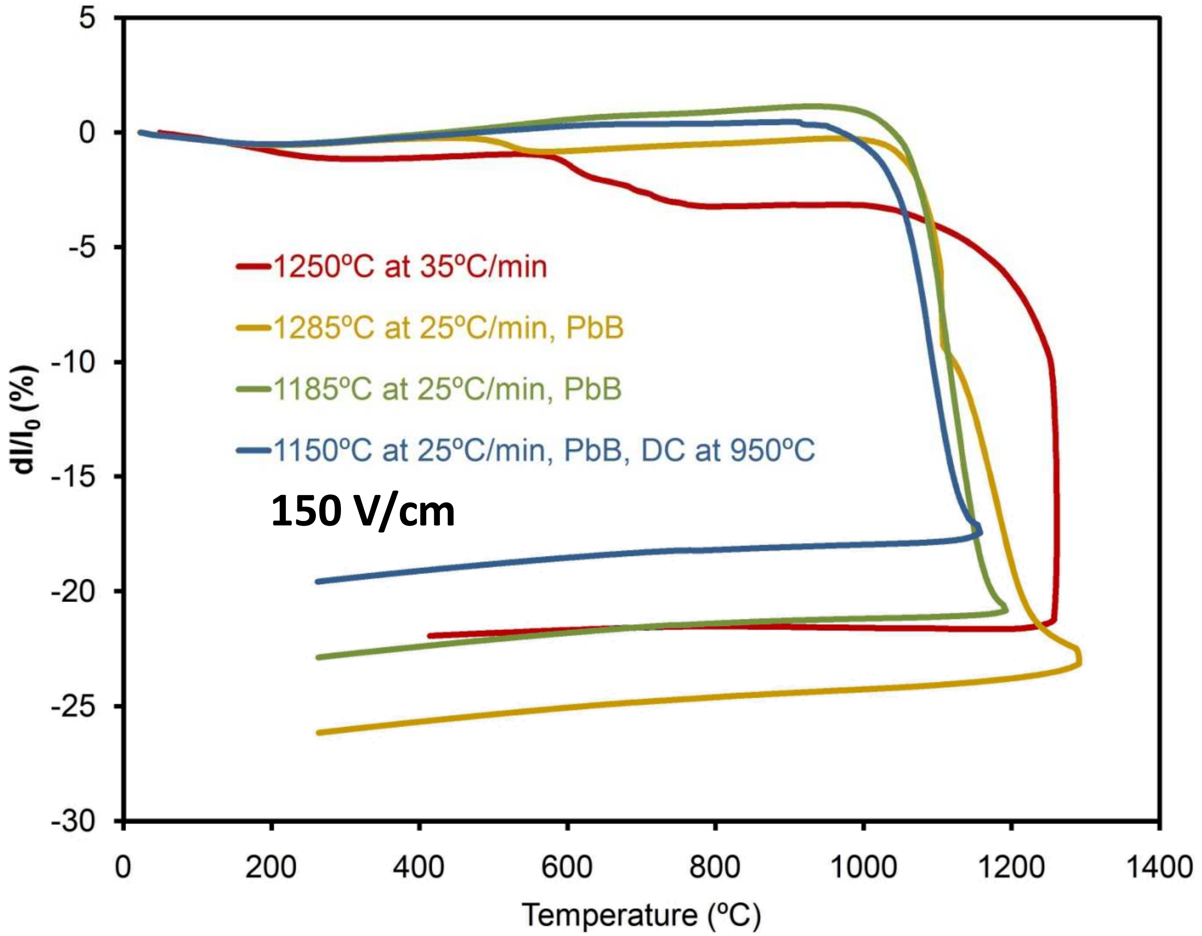
	Material properties		
Sample	**Density (g/cm3)**	**Crystal structure**	**Porosity (%)**
As Received	5.7340±0.00736	Perovskite	4.62
Sonicated	5.7341±0.00849	Perovskite	4.62

Experimental results: FAST Sintering



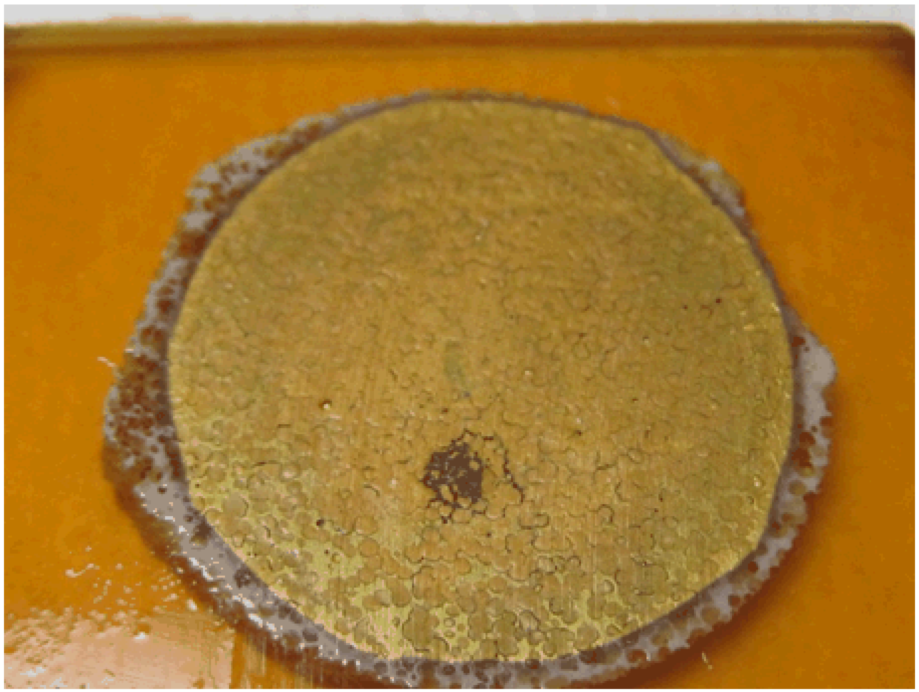
- XRD peak splitting suggests the SPS sintered bulk is tetragonal perovskite.
- In addition, the bulk density and porosity is not affected by the sonication.

Electric Field Assisted Sintering



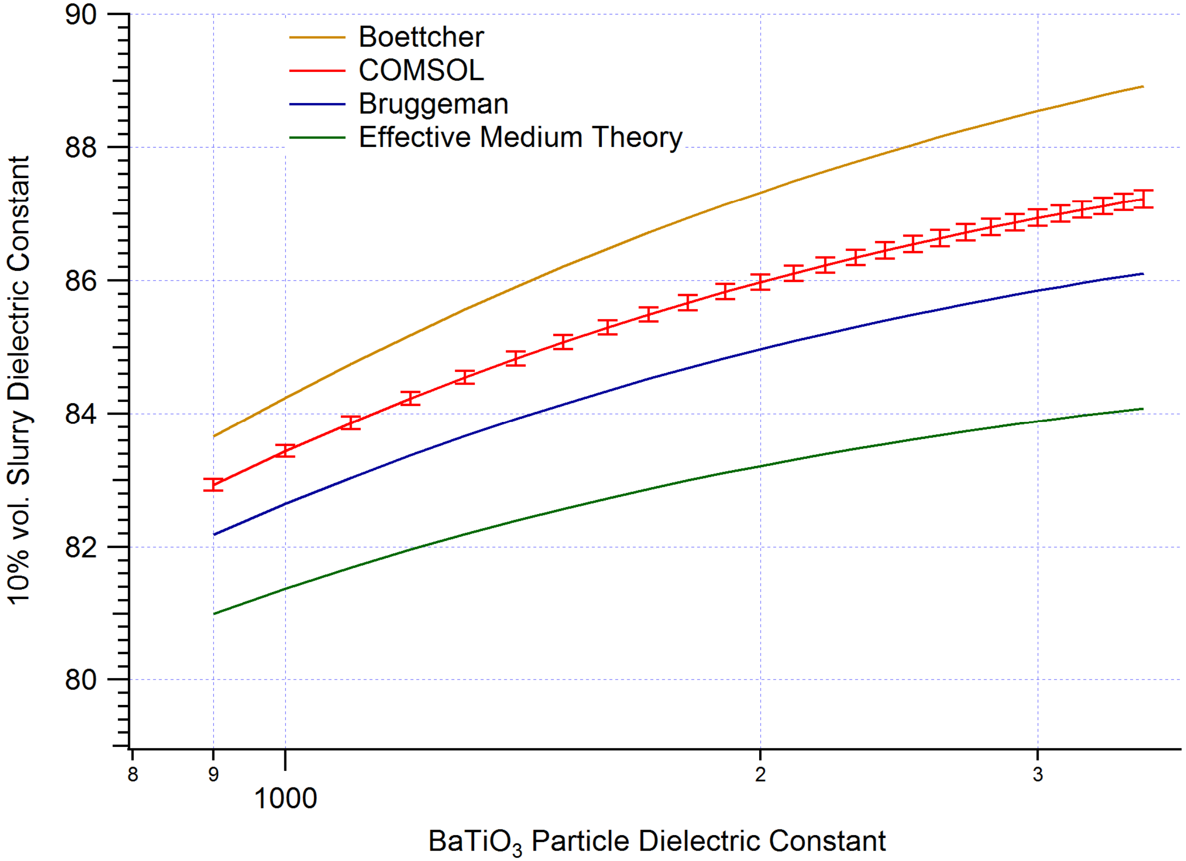
- **Higher electric fields may result in even lower sintering**
- **Temperatures similar to spark plasma sintering**

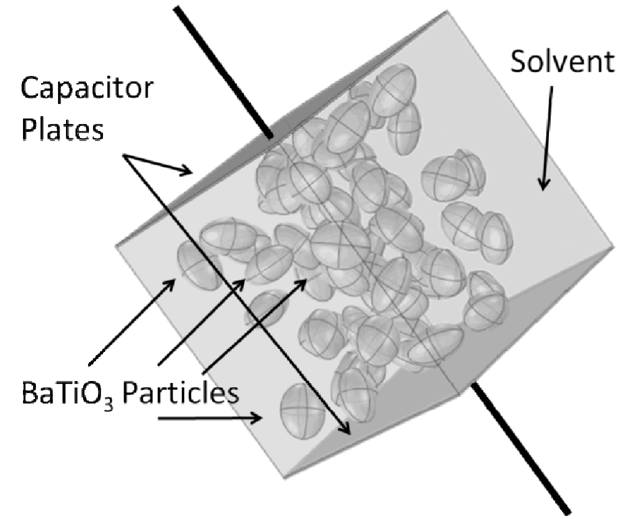
$BaTiO_3$ Reticulated Devices



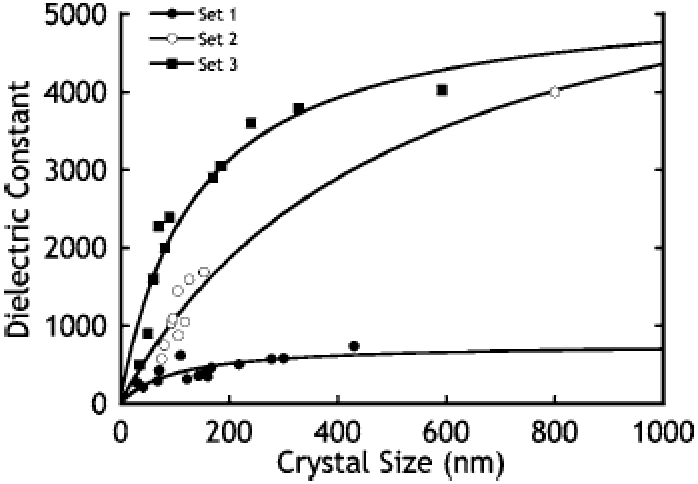
- **Replacing Masterbond epoxy with silicone**
- **Better device material properties and less defects**

Measuring Nanoparticle Permittivity in Colloidal Solution

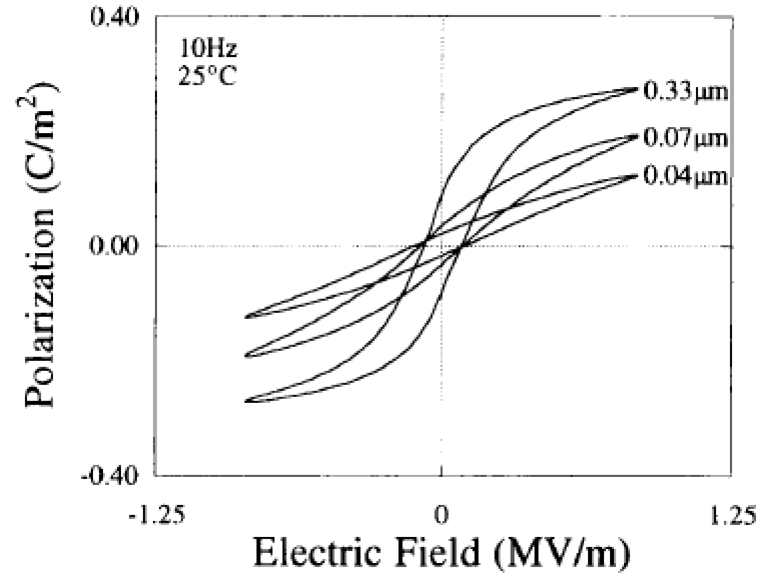




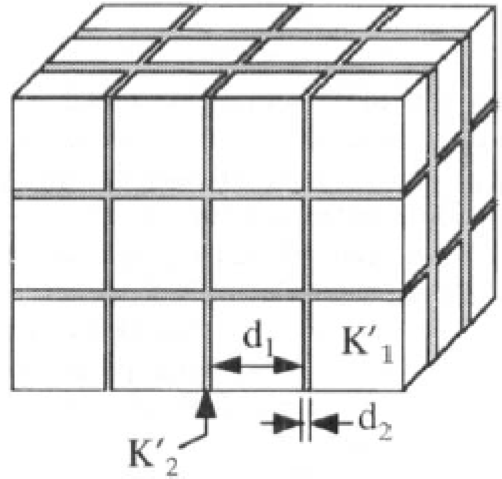
Brick Wall Model & Supporting Data



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



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



$$\frac{1}{\bar{K}'} = \frac{v_1}{K'_1} + \frac{g v_2}{K'_2}$$

FAST for Manufacturing Ceramics

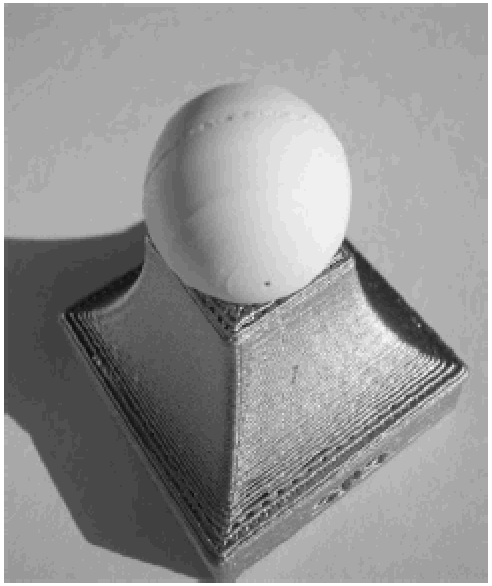


Fig. 9. Al_2O_3 sphere obtained in one single step by SPS.[63]

J. Galy, Private Communication, 2007.

Hungría et. al., Adv. Eng. Mater. Vol. 11 (2009) 616
DOI: 10.1002/adem.200900052

FAST System Manufacturers:

- **Fuji Electronic Industrial Co. (Japan)**
- **FCT Systeme GmbH (Germany)**
  - **Can make components up to 500 mm (~20”) in diameter**
- **Thermal Technology LLC (Santa Rosa, CA)**

- **Size of equipment increasing to accommodate commercial needs**
- **Technology for continuous FAST under development**
- **A large number of companies have acquired FAST but often request this info to not be made public to maintain a competitive advantage**

Sandia National Laboratories

Scalable aqueous PLZT synthesis route

- Pb $(NO_3)_2$ + $ZrO(NO_3)_2$
- La_2O_3 dissolved in HNO_3
- Diluted $Ti(OPr)_4$
- 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

Non-Provisional Patent Filed