Final Presentation

Development of $BaTiO_3$ Ceramic High Dielectric Pellets for a Capacitor using a Solid State Synthesis method involving Hand Milling, Calcining, Pressing and Sintering

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Introduction (Overview)

- $BaTiO_3$ is a widely used dielectric in capacitors due to its high dielectric constant and permittivity.
- Perovskite crystal structure (ABX_3), Ba^{2+} and Ti^{4+} ions shift under an applied electric field that creates a permanent dipole moment that allows charge to be stored. (Spontaneous below Curie temp)
- For solid state synthesis of $BaTiO_3$ (hand milling, calcination, sintering) the following reaction is used (1:1)

$BaTiO_3$ = 233.192 g/mol
$BaCO_3$ = 197.336 g/mol
TiO_2 = 79.866 g/mol

$$10\ g\ BaTiO_3 \times \frac{1\ mol\ BaTiO_3}{233.192\ g} \times \frac{1\ mol\ BaCO_3}{1\ mol\ BaTiO_3} \times \frac{197.336g}{1\ mol\ BaCO_3} = 8.462\ g\ BaCO_3$$

$$10\ g\ BaTiO_3 \times \frac{1\ mol\ BaTiO_3}{233.192\ g} \times \frac{1\ mol\ TiO_2}{1\ mol\ BaTiO_3} \times \frac{79.866g}{1\ mol\ TiO_2} = 3.425\ g\ TiO_2$$

$$BaCO_3 + TiO_2 \rightarrow BaTiO_3 + CO_2$$

Abstract

Using an equimolar ratio of $BaCO_3$ and TiO_2 that was hand milled to achieve to a particle size of less than 750 nm, calcined for 4 hours at 950°C to form $BaTiO_3$ and pressed into pellets and sintered at 1350°C for 3 hours, we found a dielectric constant of 300 at room temperature (25°C), a density of 4.58 g/cm^3 (76% theoretical of 6.02 g/cm^3) and a grain size of about 6 µm. We also found single phase purity of the pellets. Since we expected a dielectric of 1000, a density of 5.1 g/cm^3 and a grain size of less than 1µm we determined the root cause of not meeting these expected values to be non uniform particle size which created inhomogenous regions and non equimolar combination of precursors that led to porosity that lowered the dielectric constant.

Design of Experiment

- We are testing particle size, phase purity, density, grain size, and density. The first 2 of these are observations rather than factors for our experiment. Three remaining factors to examine are density, grain size, and density.
- Based on a 2^3 factorial experiment (MiniTab), there are 8 samples needed for this experiment total with a confidence level of 95% (α = 0.05)
  - 3 factors: dielectric constant, grain size, density
  - 2 levels: with sintering and without sintering
- By conducting experiments in the order of SEM (grain size), density, and then dielectric constant we were able to reduce the number of replicates needed from 16 to 8.

WORKSHEET 2

Full Factorial Design

Design Summary

Factors:	3	Base Design:	3, 8	Resolution with blocks:	IV
Runs:	8	Replicates:	1		
Blocks:	2	Center pts (total):	0		

Block Generators: ABC

Alias Structure

I
Blk = ABC

	C1	C2	C3	C4	C5	C6	C7
	StdOrder	RunOrder	CenterPt	Blocks	Dielectric Constant	Density	Particle Size
1	8	1	1	2	1	1	1
2	5	2	1	2	1	-1	-1
3	7	3	1	2	-1	-1	1
4	6	4	1	2	-1	1	-1
5	1	5	1	1	-1	-1	-1
6	4	6	1	1	-1	1	1
7	3	7	1	1	1	-1	1
8	2	8	1	1	1	1	-1
9							
10							

Figure 1:

Design of Experiment

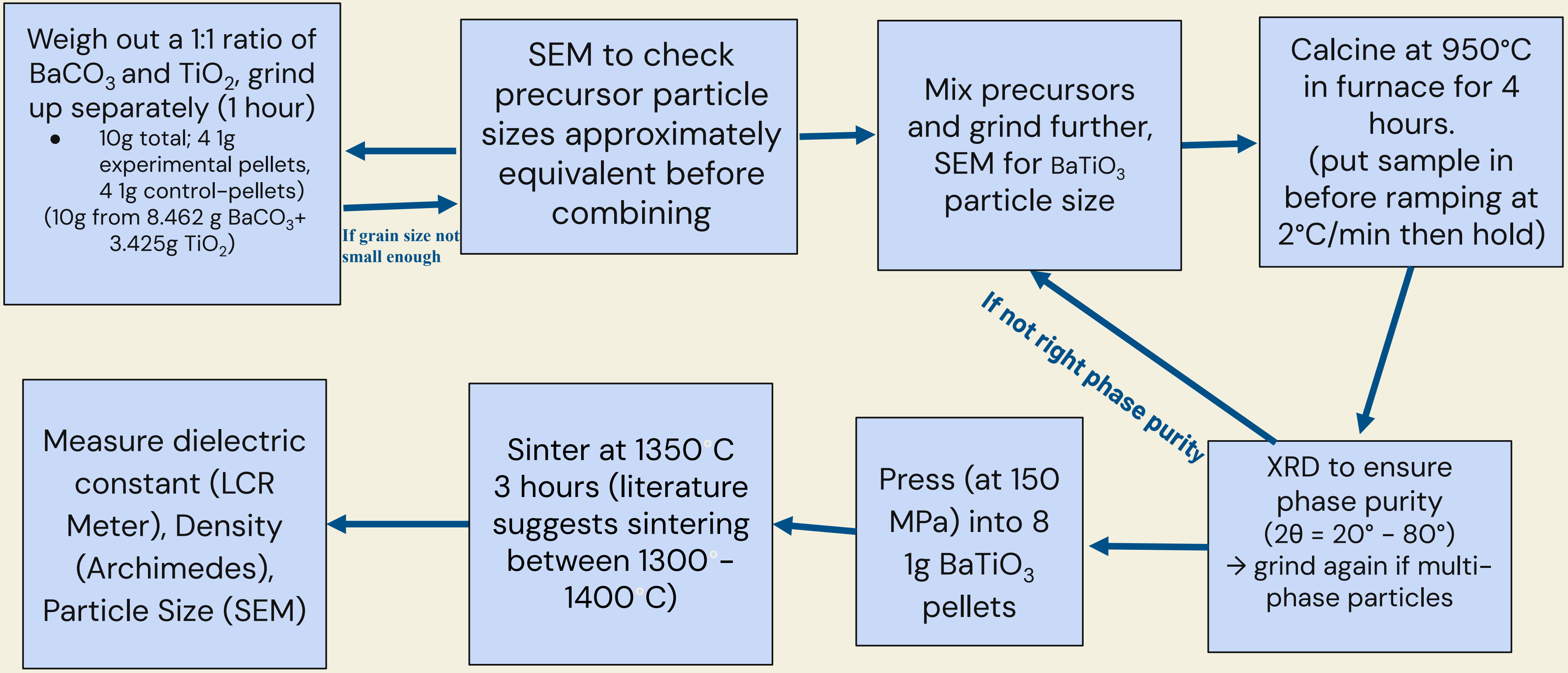
Hypotheses for **Goal Values**:

1. **Dielectric Constant** – One-Sided t test
   a. Null: $\mu_{exp} < 1000$
   b. Alternative: $\mu_{exp} \geq 1000$

1. **Density** – Two-Sided t test for 85% theoretical of 6.02 g/cm^3
   a. Null: $\mu_{exp} = 5.1$ g/cm^3
   b. Alternative: $\mu_{exp} \neq 5.1$ g/cm^3

1. **Particle Size** – One-Sided t test
   a. Null: $\mu_{exp} \geq 1$µm
   b. Alternative: $\mu_{exp} < 1$µm

Workflow- Procedure



Deviations from original proposal

- XRD for phase purity: not as phase pure as desired, but unable to calcine again due to time restraints
  - With enough time, would have re-calcined
  - Likely will result in lower density and dielectric constant than initially expected
- Furnace time ended up being larger than expected due to ramp up and down times, this increased the overall cost of the furnace by a small amount. (Sintering 350°C for 3 hours)

Particle Size of Individual Precursors

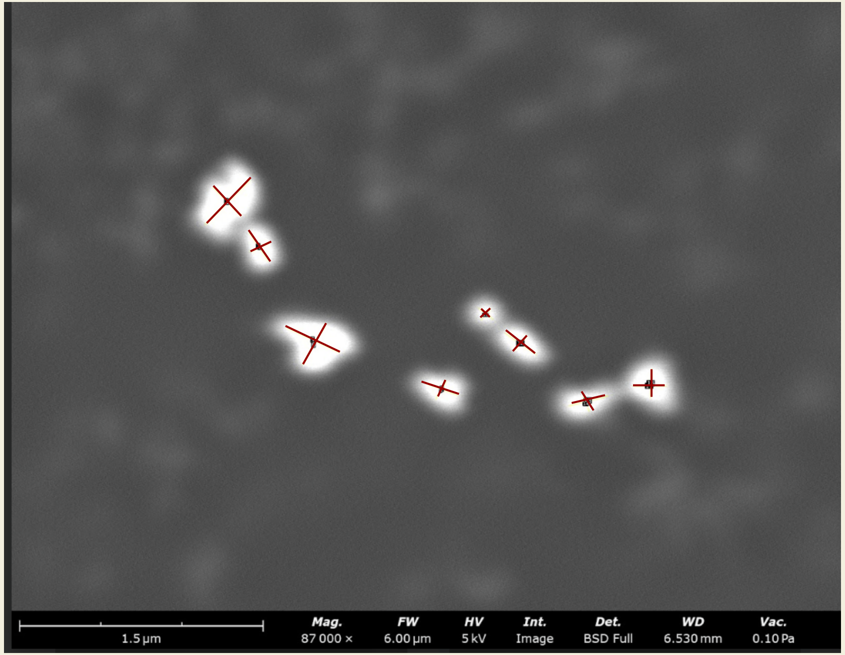


Figure 2: SEM of $BaCO_3$

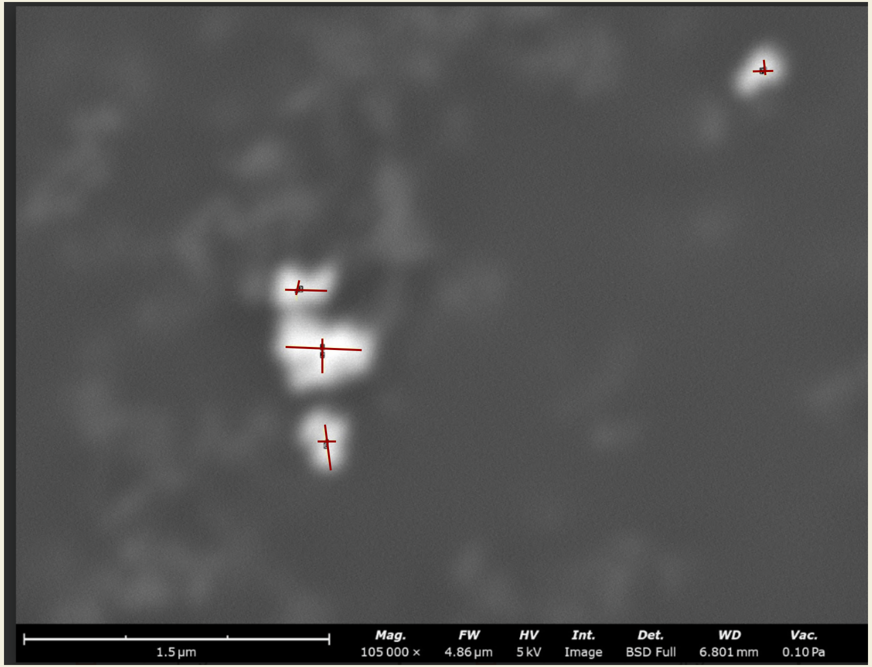


Figure 3: SEM of TiO_2

Particle Size of Individual Precursors - Methods

- 3 images were taken of each sample of $BaCO_3$ and TiO_2 and all of the particles on the image were measured (at least 5 per image)
- Each measurement consisted of an x and y distance/diameter of the particle through ImageJ
  - The x and y diameters were averaged for each particle and are shown below
  - The standard error was calculated for the total x and y data sets from: $SE = \sigma/\sqrt{n}$
    - Sigma is the standard deviation and n is the sample size

Material	Direction	Average	Standard Deviation	Variance
TiO_2	x	153.511 ± 18.5	97.71	9547.68
TiO_2	y	139.216 ± 9.3	49.15	2415.76
$BaCO_3$	x	234.381 ± 22.8	116.29	13524.25
$BaCO_3$	y	144.667 ± 21.3	104.79	10981.73

XRD Spectra of Powder – Post Calcining

After Calcining, XRD Spectra of powder matched up most peaks with expected $BaTiO_3$ with some Ba_2TiO_4 peaks as a byproduct formed during calcination. Ba_2TiO_4 has a dielectric constant of 40 when synthesized via solid state methods and this may have affected our final values for dielectric constant.[1]

$BaTio_3$ Cubic: 17.3%

$BaTio_3$ Tetragonal: 64.5%

Ba_2TiO_4: 18.2%

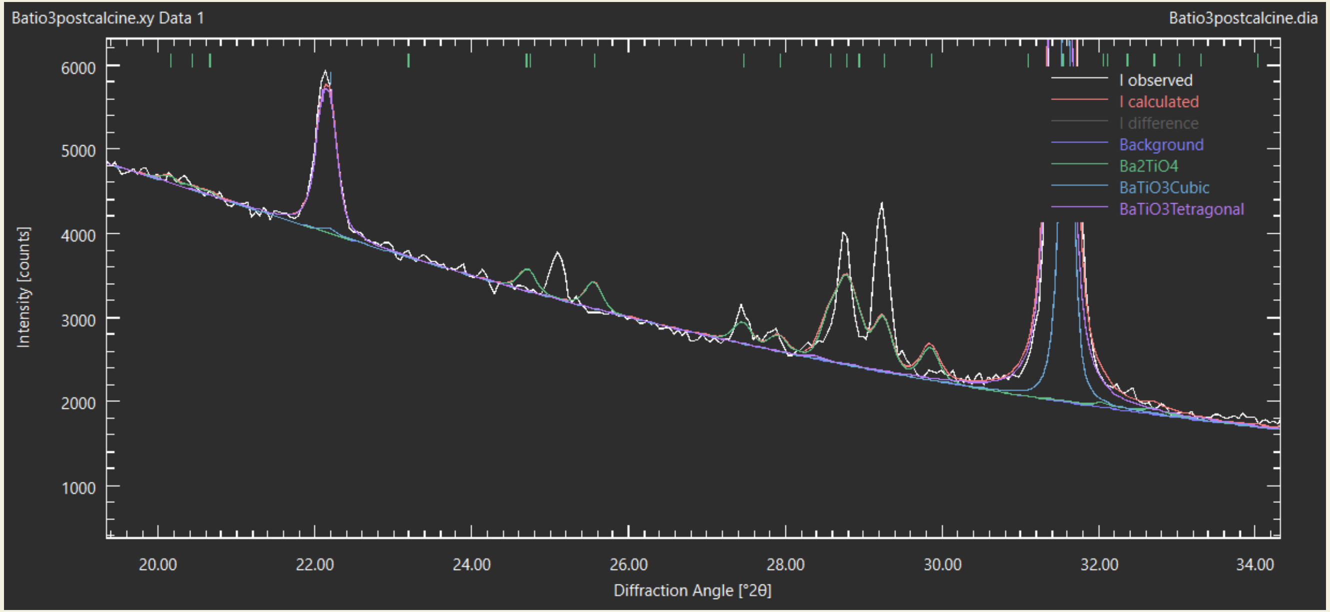


Figure 4: Profex image of XRD after calcination process

XRD Spectra – Post Calcining

- 64.5% tetragonal in red spectra

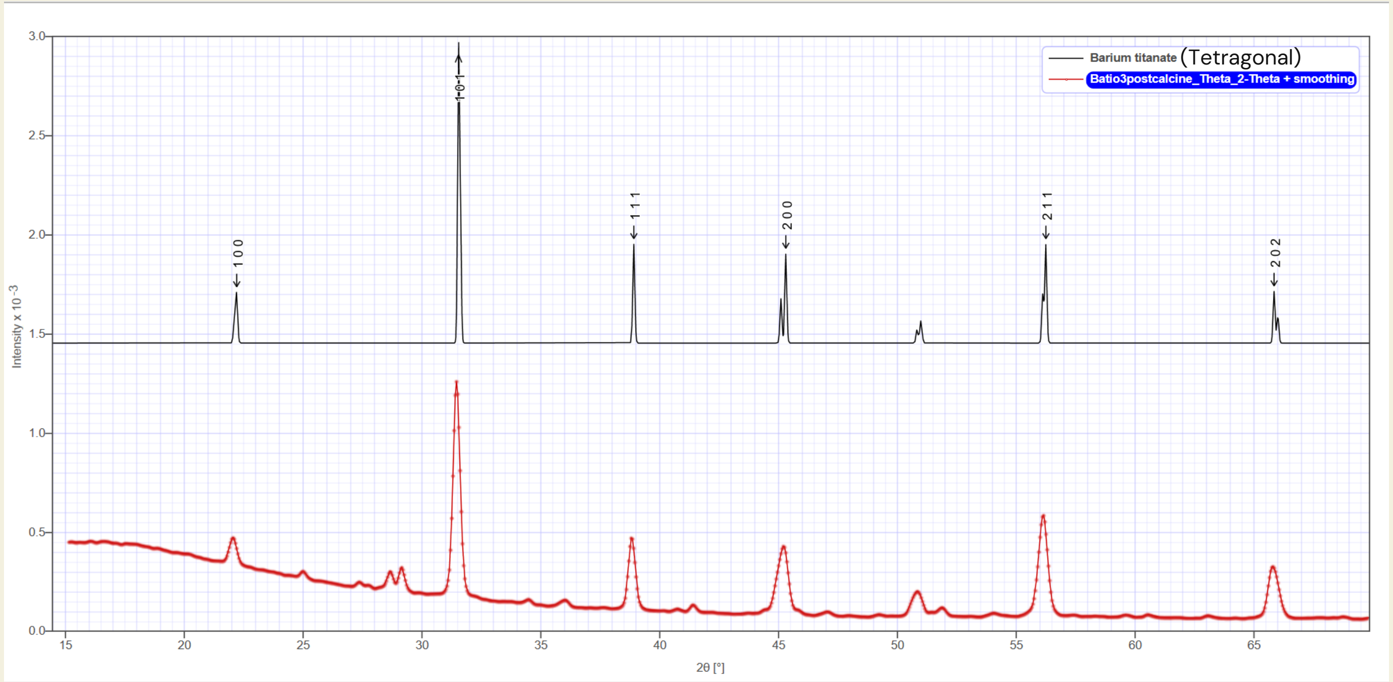


Figure 5: XRD of sample overlaid with CIF file after calcining

XRD - Post Sintering

- ❖ Post-sinter XRD results are inconclusive due to researcher error.
- ❖ The black spectra is not representative of the post-sintered pellet

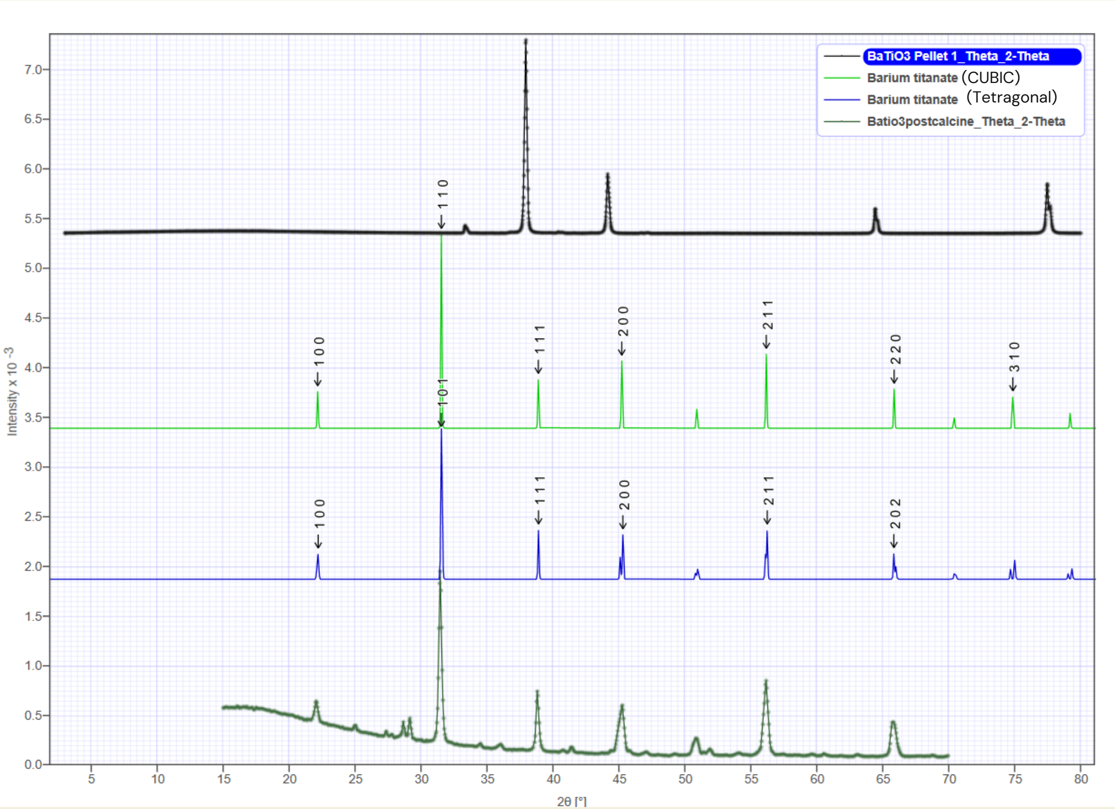


Figure 6: XRD overlay comparing our samples (pre & post sintered) to crystallography cif files

Density and Porosity of Pellets

Pellet	Archimedes Density (g/cm³)	Theoretical Density (g/cm³)	Porosity (%)
1	Sheared	Sheared	Sheared
2	1.925 ± 0.46	4.739 ± 0.22	59.368 ± 7.74
3	4.949 ± 0.46	4.638 ± 0.22	6.712 ± 7.74
4	5.657 ± 0.46	4.657 ± 0.22	21.475 ± 7.74
5	5.036 ± 0.46	4.577 ± 0.22	10.027 ± 7.74
6	4.656 ± 0.46	3.361± 0.22	38.542 ± 7.74
7	5.080 ± 0.46	5.065 ± 0.22	0.289 ± 7.74
8	4.808 ± 0.46	3.883 ± 0.22	23.817 ± 7.74
Average	**4.587 ± 0.46**	**4.417 ± 0.22**	**3.854 ± 7.74**
Standard Deviation	1.22	0.59	20.48
Variance	1.48	0.34	419.42

Table 2: Density and porosity values for each pellet

Archimedes:

$\rho = (m_{air}) \ / \ (m_{air} - m_{ethanol}) * \rho_{ethanol}$

Bulk:

Vol. of pellet is $\pi(R^2)(t)$

R is radius, t is thickness of pellet

So $\rho_{bulk} = (m_{air}) \ / \ \pi(R^2)(t)$

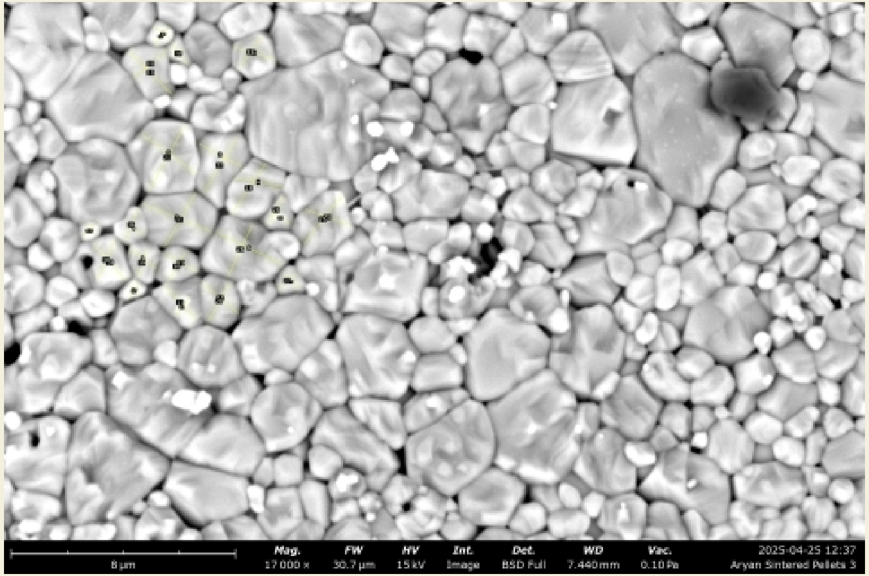
Porosity:

$1 - (\rho_{bulk} / \rho)$

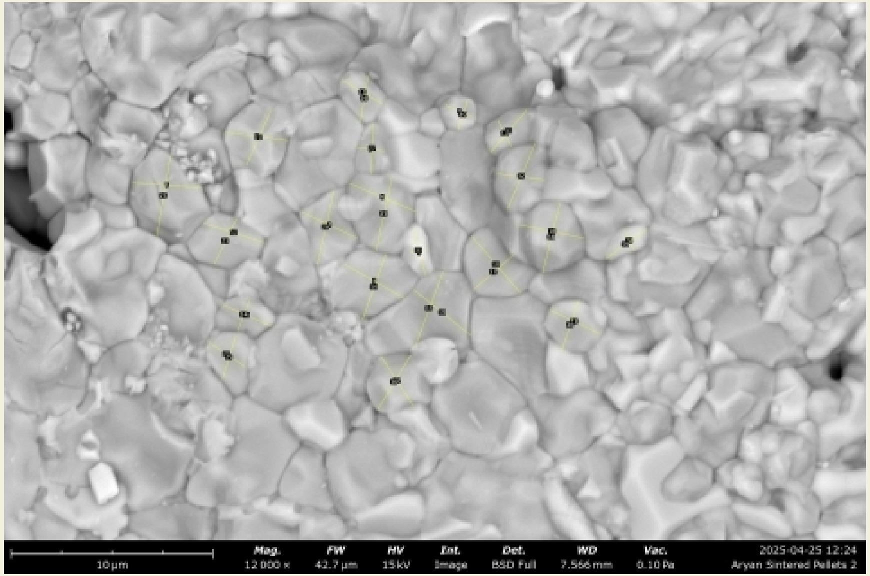
Percent Theoretical:

(4.587/6.02)*100% = 76.2% Theoretical Density

Grain Size (SEM)



Figures 8: Annotated images of the polished pellet surface under the SEM



Figures 9: Annotated images of the polished pellet surface under the SEM

Grain Size (SEM)

- 4 pellets were imaged under SEM. 3 images were taken per sample, and within each image at least 15 measurements were made
- Each measurement consisted of an x and y distance/diameter of the grain through ImageJ
  - The x and y diameters were averaged for each pellet and are shown below
  - The standard error was calculated for the total x and y data sets from: $SE = \sigma/\sqrt{n}$
    - Sigma is the standard deviation and n is the sample size

Sample	Average X (μm)	Average Y (μm)
1	6.877	6.7809
2	4.28062963	4.289074074
3	4.314695652	4.667326087
4	3.815103448	3.38637931
Average	4.821857183	4.780919868

Table 3: Average grain size of pellets

Dielectric Constant (LCR Agilent 4284A LCR Meter)

Pellet	Dielectric	Standard Deviation	Variance
2 - Front	339.1 ± 1.49	3.64	13.26
2 - Front	338.61 ± 1.49		
2 - Front	335.32 ± 1.49		
2	331.79 ± 1.49		
2	330.81 ± 1.49		
2	331.91 ± 1.49		
4 - Front	222.45 ± 1.80	4.41	19.44
4 - front	214.25 ± 1.80		
4 - front	213.49 ± 1.80		
4	212.23 ± 1.80		
4	211.34 ± 1.80		
4	210.08 ± 1.80		
5 - front	345.26 ± 0.66	1.63	2.65
5 - front	345.26 ± 0.66		
5 - front	345.66 ± 0.66		
5	345.26 ± 0.66		
5	342.43 ± 0.66		
5	342.03 ± 0.66		
Average	**297.63 ± 14.4**		

Table 4: Dielectric values for 3 pellets

- Out of the 7 pellets that did not shear, 3 of them were deemed best for LCR testing due to them being the most planar and clean (polished).
- Dielectric Constant (κ) was calculated using the formula below:

$$\kappa = C * t / (\varepsilon_0 * A)$$

- C is Capacitance
- t is thickness of pellet
- A is Area of Contact (Pellet)
- ε_0 is vacuum permittivity

Data Analysis - Dielectric Constant

- One-sided t-test conducted with a focus on the right tail in MATLAB
- Null hypothesis failed to be rejected
  - With a 5% confidence interval, we did not achieve the goal dielectric constant
- Percent error calculation: 70.237% error

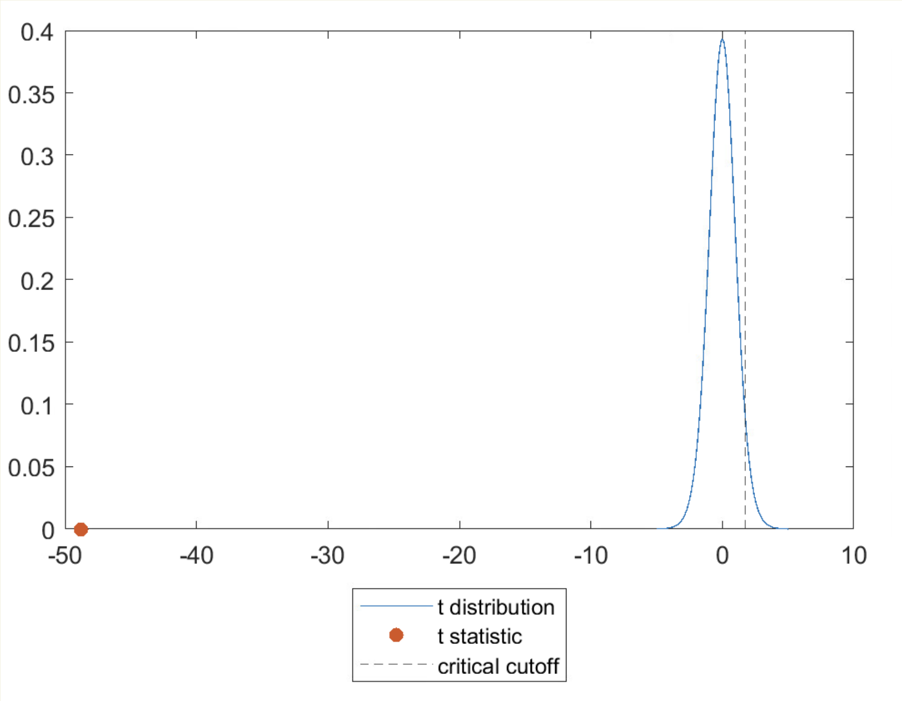


Figure 10: T-test graph for the dielectric constant

Data Analysis - Density

- Two-sided t-test conducted in MATLAB
- Null hypothesis failed to be rejected
  - With a 5% confidence interval, we did not achieve the goal density
- However, percent error reveals:
  - 10.05% error from the goal mean
  - 76.2% of total theoretical density

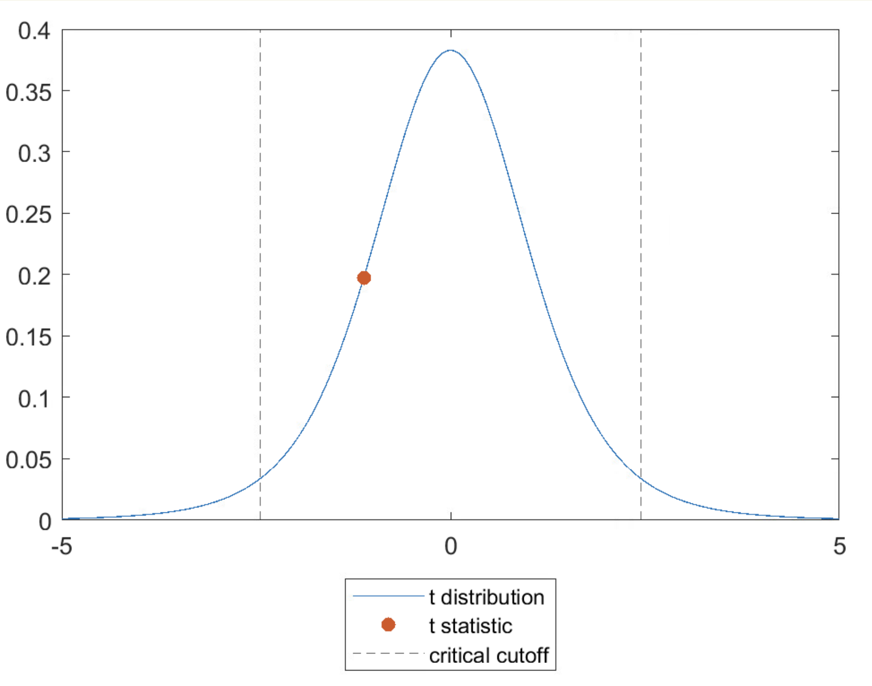


Figure 11: T-test graph for the density of pellets

Data Analysis – Grain Size

- ❖ One-sided t-test conducted with a focus on the left tail in MATLAB
- ❖ Null hypothesis failed to be rejected
  - ➢ With a 5% confidence interval, we did not achieve the goal grain size

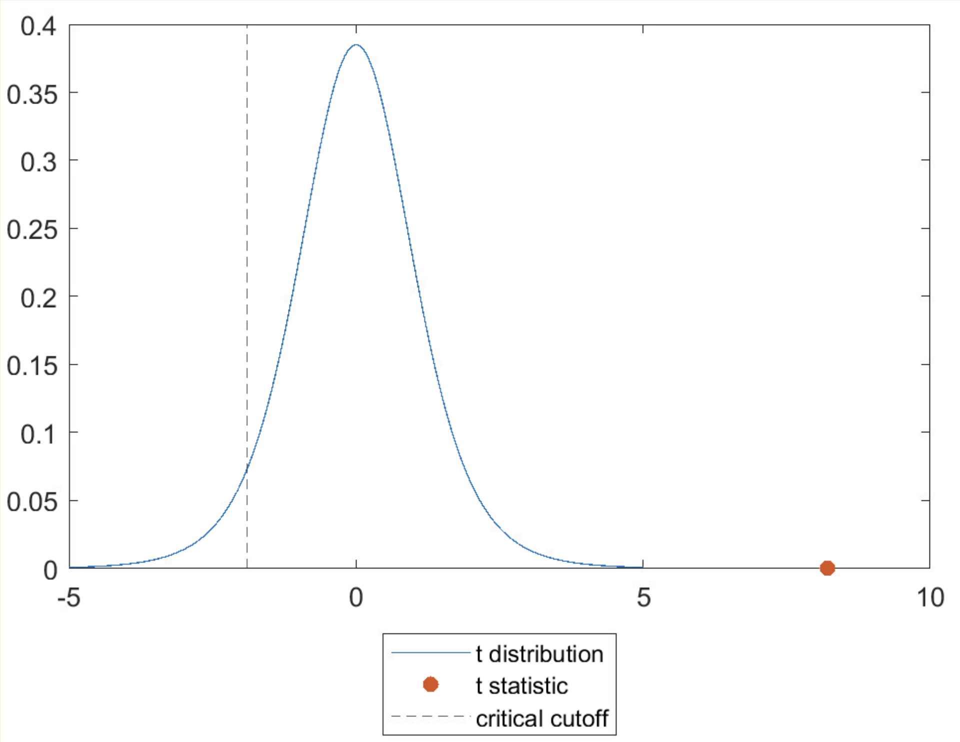


Figure 12: T-test graph for the grain size of pellets

Final Parameters

	Value	Pass or Fail
Density	4.58 g/cm^3	Fail (76% of expected) **Expected: 5.1 g/cm^3**
Dielectric Constant	300	Fail (30% of expected) **Expected: 1000**
Grain Size	6.34 μm x 7.00 μm	Fail (600% of expected) **Expected: 1μm**

Root Cause Analysis:

- Inconsistent particle size with a variation of _ for BaCO3 and _ for TiO2 led to imperfect phase growth.
    - **$BaTio_3$ Cubic:** 17.3%, **$BaTio_3$ Tetragonal:** 64.5%, **Ba_2TiO_4:** 18.2%

- The imperfect phase distribution led to uneven grain sizing post sintering
    - Uneven grains lead to increased porosity
- Due to reduced phase purity and uneven grain growth from uneven precursor particle, the dielectric constant was drastically reduced to 300.

Amended Budget (Final Costs)

Material/Equipment	Amount/Usage	Cost ($)
$BaCO_3$	8.462 (g)	0.42
TiO_2	3.425 (g)	0.31
Weighing Scale	-	-
Mortar and Pestle	1 (week)	100
Furnace	46.5 (hours)	1162.5
Hydraulic Press	2 (hours)	50
SEM	2 (hours)	80
XRD	2 (hours)	140
Agilent 4284A LCR Meter	–	–
Density Determination Kit (ethanol)	–	–
Miscellaneous	-	0

Table 5: Amended budget values

	Expected	Actual
Total Cost	$1,550.73	$1,533.23
Price per Pellet	$193.84	$219.03

- ❖ Total cost was lower than expected by $17.50
- ❖ Since 1 pellet sheared, only 7 successful pellets made
    - ➢ Cost per pellet higher than expected by $25.19

Future Recommendations

- Improve techniques used
  - Improve hand milling technique: Standardize grinding time, pressure, and motions during hand milling to achieve **finer and more uniform particle sizes.**
  - Handle powders and pellets carefully: Minimize contamination and mechanical damage during transfers, especially before sintering.
  - Enhance pressing techniques: Apply more consistent pressure and polish pellet surfaces better to improve dielectric measurements.
- Perform additional tests
  - Additional XRD, possibly TGA, DSC, or other tests to help determine phase purity
- Reassess heat-treatment parameters: ie. experiment with slightly lower sintering temperatures (1300–1325°C) or shorter times to prevent abnormal grain growth.
  - Recalcine to achieve highest possible phase purity of tetragonal phase
- Another possibility for a future experiment could be the addition of dopants to increase dielectric constant
  - Lanthanum or Strontium

References

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