

Investigation of Annealing Condition Effects on Impedance of Barium Titanate Ferroelectric Ceramic

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Abstract

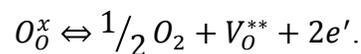
The effects of annealing conditions on barium titanate electroceramics are investigated with scanning electron microscopy and DC resistance measurements. Barium titanate ceramic samples were synthesized using pressureless sintering (PS) and spark plasma sintering (SPS) methods and then annealed in various atmospheres to provide either reducing or oxidizing conditions for the samples, in the hopes of creating a range of defect chemistries and observable trends in electrical properties. We report that the chosen annealing conditions resulted in anomalously high DC resistivities in PS samples with a single oxidized sample exhibiting a resistivity of $2.93 \text{ M}\Omega \text{ m}^{-1}$, and the remainder of the samples exhibiting resistivities of above $25 \text{ M}\Omega \text{ m}^{-1}$. SPS samples exhibited a resistivity of $1203 \text{ }\Omega \text{ m}^{-1}$. High PS sample resistivities indicate that future samples processed via pressureless sintering should be further reduced via increased annealing temperatures and treatment times.

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Introduction

BaTiO₃ (BT) is a widely used ferroelectric ceramic with a perovskite crystal structure that exhibits excellent piezoelectric¹ and dielectric properties². As such, BT is the dielectric material of choice for many multi-layer ceramic capacitors (MLCCs)³⁻⁹, in which hundreds of dielectric layers and internal electrodes are alternately stacked^{3,7} to provide high capacitance per unit volume^{3,7}. MLCC's are important new components in ever-shrinking electronic circuits. During production of MLCCs, metallic electrodes, both internal and external, such as Ni^{4,7,9,10} and Cu⁶ are often sintered in the same step as BT-base layers, leading to the use of reducing sintering atmospheres to avoid electrode oxidation^{3,4,6,10}. The reducing sintering environment contributes to defect creation in the BT-based layers, most notably oxygen vacancies and transitions from Ti⁴⁺ to Ti³⁺ ion valences^{8,10}.

Multiple groups report the reducing or oxidizing nature of the sintering or annealing atmosphere, characterized chiefly by oxygen partial pressure, denoted $p(O_2)$, is directly correlated with the creation of defects like oxygen vacancies^{3,4,9-11}. Oxygen vacancies directly effect BT sample permittivity and resistivity^{4,9,11}. Specifically, Choi, et al. described the process by which oxygen vacancies clamp ferroelectric domain wall motion, leading to degradation in both dipole and ionic permittivity^{4,9}. Oxygen vacancies are n-type defects that increase sample conductivity⁵. It is modeled that in reduced samples there will be an increase in oxygen vacancies according to the defect reaction^{3,9,11}:



The concentration of such defects at electrode/ceramic interfaces is thought to be the main cause of failure in MLCCs, by oxygen vacancy migration to cathode/ceramic interfaces⁴. In order to lower the concentration of the oxygen vacancies in the dielectric layers, the sintered BT samples

have often been heat treated at lower temperatures in oxidizing atmosphere to re-oxidize the samples^{3,6}. The effects of re-oxidation steps in MLCCs are less widely reported. As MLCC processing techniques evolve, it is thus of interest to attempt to investigate the effects of annealing conditions, including temperature, atmosphere, and time, on BT ceramic sample properties.

The purpose of this investigation was to synthesize an array of BT ceramic samples via pressureless sintering (PS) and spark plasma sintering (SPS) methods and anneal those in reducing and oxidizing atmospheres to create a range of defect chemistries. The goal of creating samples with variable defect chemistries was to observe trends in resistivity and impedance values among the samples, as well as critical conditions within those trends. We report that the chosen annealing conditions resulted in anomalously high DC resistivities in PS samples with a single oxidized sample exhibiting a resistivity of $2.93 \text{ M}\Omega \text{ m}^{-1}$, and the remainder of the samples exhibiting resistivities of above $25 \text{ M}\Omega \text{ m}^{-1}$. The SPS treated sample showed a markedly smaller resistivity than the PS samples, with a value of $1203 \text{ }\Omega \text{ m}^{-1}$. Impedance measurements were inconclusive and will be investigated further.

Methods and Materials

Pressureless Sintering (PS)

High-surface area powder BaTiO_3 (99+%, Alfa Aesar) was pressed to form cylindrical pellets. To give each pellet its initial geometry, 0.6 grams of BT powder was pressed uniaxially using a Specac 10 mm cylindrical pressing die in a Carver Model #3912 hydraulic press under a 1 ton applied load for 3 minutes. Then, the pellets were isostatically pressed in a Fluitron Cold Isostatic Press at 225 MPa of pressure for 3 minutes. All green pellets were then sintered in air at 1275°C for 2 hours.

Spark Plasma Sintering (SPS)

Micron-sized BT powder (Alfa Aesar, 99+%) was ball-milled to create nanometer range particle sizes, and sintered via the spark plasma sintering (SPS) method¹². During SPS processing, these samples were raised from room temperature to 800° C at a heating rate of 200°C/min, from 800°C to 900°C at 100°C/min, and 900°C to the final sintering temperature of 1000°C at a rate 50°C/min. The samples were held at the sintering temperature for 5 minutes, then cooled at a rate of 100°C/min. The maximum voltage and current were 3 volts and 800 amperes respectively. Sintering was performed under an applied uniaxial pressure of 20 MPa with a 20-mm diameter pressing die.

Annealing Conditions

To create an array of defect chemistries in the BT samples, sintered pellets were polished and then annealed for 6 or 12 hours at 800°C in varying annealing atmospheres. The atmospheric conditions produced either reducing or oxidizing annealing conditions. In order to create reducing atmospheres, samples underwent annealing under flowing 95% Ar/ 5% H₂ gas at 200 SCCM. A single set of samples was annealed in a low-pressure reducing environment of 1.26 torr of stagnant air at 1000°C for 12 hours. Samples undergoing oxidizing conditions underwent heat treatment under flowing O₂ gas at 200 SCCM. A control sample underwent no heat treatment and its properties were measured as sintered. SPS samples were annealed in a reducing atmosphere of 95% Ar/ 5% H₂ gas flowing at 200 SCCM at 800° C for 6 hours.

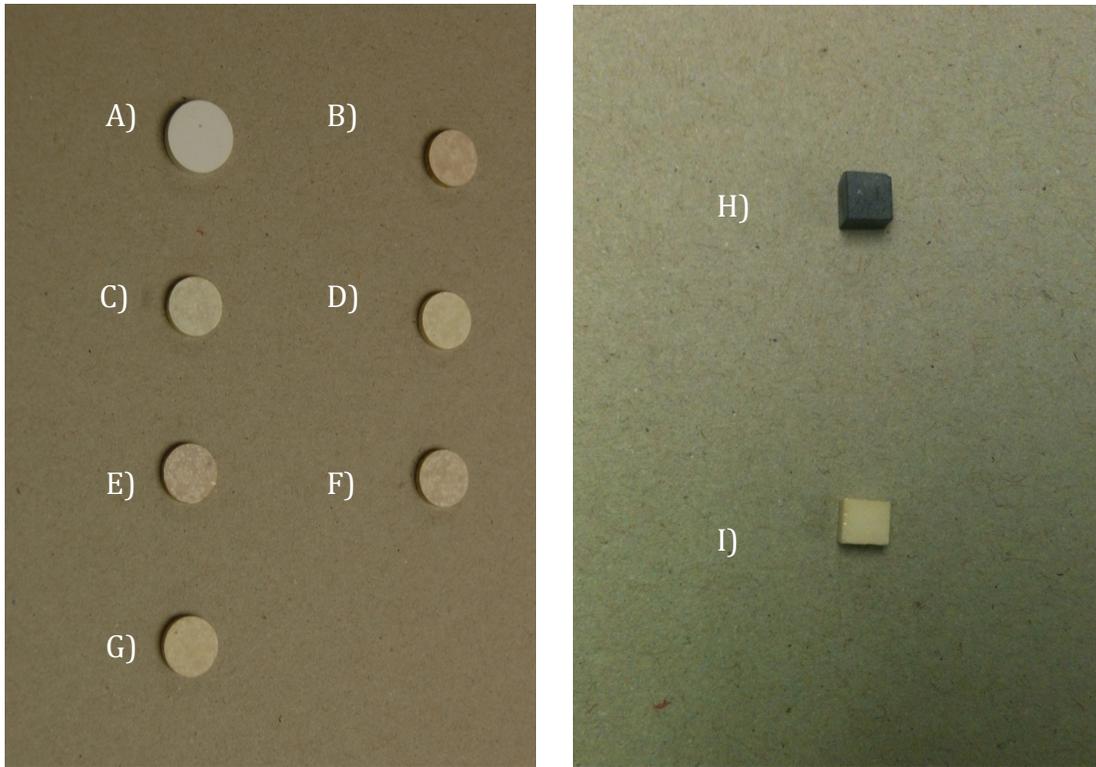


Figure 1.

One sample per PS sample set in left image: A) Pressed green BT pellet, B) Sintered pellet prior to annealing (control sample), C) 5 % H₂/ 95% Ar, 200 SCCM, 6 hrs, 800 °C, D) 5 % H₂/ 95% Ar, 200 SCCM, 12 hrs, 800 °C, E) O₂, 200 SCCM, 6 hrs, 800°C, F) O₂, 200 SCCM, 12 hrs, 800°C, G) Vacuum pumped to 1.26 torr, 12 hrs, 1000°C, stagnant air.

SPS procedure samples in right image: H) As sintered (control sample), I) Annealed in Air, 200 SCCM, 1050°C, 12 hrs

Scanning electron microscopy (SEM, JEOL 6335F FEG-SEM) was performed to characterize starting powders and sintered ceramic microstructures. For electrical measurements, a thin layer (~10 nm) of gold (Au) was sputter coated and Ag paste (Ted Pella, Leitsilber 200 Silver Paint) was applied to parallel faces of both the PS and SPS samples. Using a standard ohmmeter, the average DC resistances of both SPS and PS BT samples were measured. Resistivity was calculated using resistance values and sample dimensions according to the resistivity formula:

$$\rho = \frac{RA}{L}$$

where ρ is resistivity, R is measured sample resistance, A is the area of the parallel faces with electrodes applied and L is the thickness of the samples. Electrochemical impedance spectroscopy (EIS) was performed to analyze impedance in the PS samples (Solartron SI 1260 Impedance/Gain-Phase Analyzer).

Results and Discussion

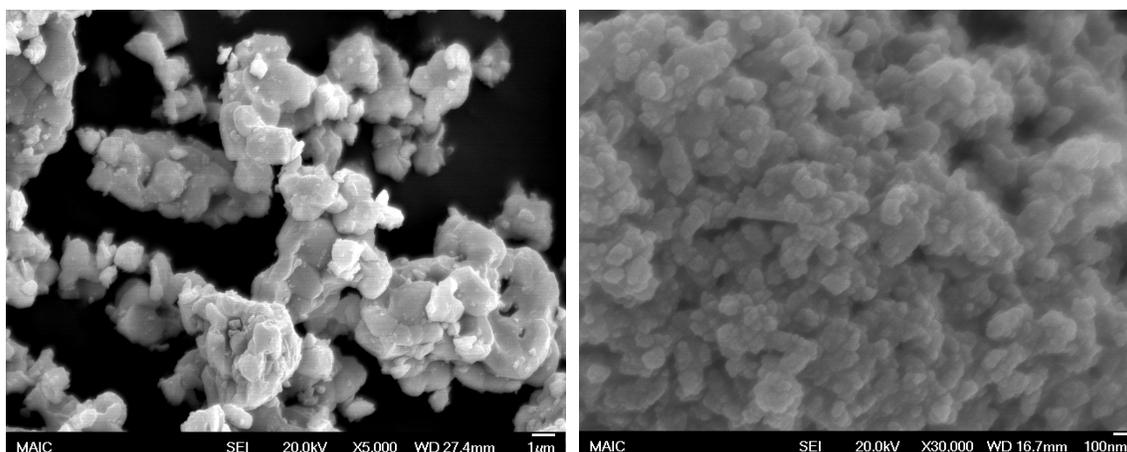


Figure 2. Left image: Micron starting powders for SPS samples, pre-ball milling. Average particle sizes are $\sim 1 \mu\text{m}$. Right image: Powder after 75 hour ball-milling, with average particle sizes on the order of 100 nm.

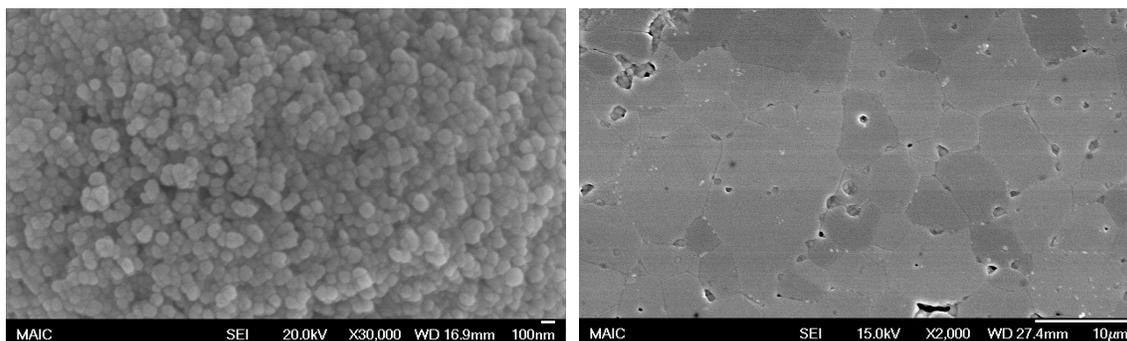


Figure 4. Left image: High surface area starting powders for PS samples. Average particle sizes are $\sim 100 \text{ nm}$. Right image: PS BT sample microstructure indicating grain sizes between 5 and 20 μm .

SEM Characterization

The pre- and post-ball milling starting powders for the SPS samples are shown in Fig 2. The left image of Fig. 3 shows SEM imagery of PS starting powders. Nanometer-sized starting

powder particle leads to high densification and fine grain sizes, and BT ceramic permittivity is a maximized as grain size decrease to a phase-imposed lower limit of about $.8 \mu\text{m}^2$. The right image in Fig. 3 depicts a representative microstructure of the PS BT, with grain sizes between 5 and 20 μm across. These fine grain sizes are the most reliable microstructure in terms of MLCC performance⁷. Consistent microstructures in the PS samples eliminate variability in grain size, which is a major factor effecting BT sample permittivity^{2,8,9,11}.

Electrical Properties

Sinter Process	Annealing Conditions	Resitivity ($\Omega \cdot \text{m}$)
PS	None (Control)	> 2.52E+07
PS	O ₂ , 200 SCCM, 6 hrs, 800°C	2.93E+06
PS	O ₂ , 200 SCCM, 12 hrs, 800°C	> 2.48E+07
PS	5 % H ₂ / 95% Ar, 200 SCCM, 12 hrs, 800 °C	> 2.50E+07
PS	5 % H ₂ / 95% Ar, 200 SCCM, 6 hrs, 800 °C	> 2.53E+07
PS	Vacuum pumped to 1.26 torr, 12 hrs, 1000°C, stagnant air	> 2.55E+07
SPS	None (Control)	1203
SPS	Air, 200 SCCM, 12 hrs, 1050°C	> 6.3E+06

Table 1. Sintering Process, Annealing Conditions, Resistance and Resistivity Measurements of Barium Titanate Ceramic Synthesized by PS and SPS Techniques

As seen in Table 1, PS BT samples that underwent heat treatments all exhibited resistivities of $25 \text{ M}\Omega \text{ m}^{-1}$ and above, with the exception of the set of samples annealed under slightly oxidizing conditions of flowing O₂ gas for 6 hrs. This set of slightly oxidized samples exhibited a resistivity of $2.93 \text{ M}\Omega \text{ m}^{-1}$. The spark plasma sintered samples were significantly reduced during the SPS procedure itself, as indicated by color change⁸ from white powder to a black sample upon sintering, seen in sample (H) in Fig. 1, and showed a markedly smaller resistivity than the PS samples, with a value of $1203 \Omega \text{ m}^{-1}$. The SPS samples show that spark

plasma sintering drastically reduces samples, as both sintering methods begin with starting powders of the same material with comparable particle sizes and the SPS samples had resistivities ten thousand times smaller than the PS samples. The high resistivities in both the control and reducing-atmosphere treated samples indicates that the reducing treatment did not succeed in forming excess oxygen vacancies, which would have lowered sample resistivities in the reduced samples versus the control. EIS measurements were inconclusive due to the high resistance exhibited by the PS samples.

Conclusion

Resistivity in the $25 \text{ M}\Omega \text{ m}^{-1}$ range and above in the majority of PS sintered samples indicates that future samples processed via pressureless sintering should be further reduced by increasing annealing temperatures, treatment times, and subjecting them to stronger reducing conditions. Unfortunately, with the current array of samples, it remains impossible to discern trends in either resistivity or impedance.

Many routes remain to fully take advantage of the already processed samples and complement them with further processing trials in order to further investigate annealing condition effects on BT sample properties. A set of 6-hour and 12-hour, 1000°C PS samples, already in progress, will provide insight into the role of annealing temperature at set anneal times and atmospheres. Resistivity measurements of these 1000° samples should also indicate whether a processing flaw led to the high values of resistivity in the 800° samples or alternatively, the chosen conditions were insufficient to create measurably reduced and oxidized samples. Also, EIS measurements of the reduced SPS samples should provide impedance data that will set a benchmark for comparison to future reduced samples.

Based on the previously discussed work of Choi, et. al^{4,9}, future samples should take advantage of measurable $p(\text{O}_2)$ to quantify reducing and oxidizing atmospheric conditions and confirm the correlation of permittivity and resistivity to oxygen partial pressure. Monitoring of $p(\text{O}_2)$ with an oxygen probe during annealing will also lead to optimized combinations of gas to flow during annealing treatments and thus lead to more precise control of reducing and oxidizing atmospheres.

Acknowledgment

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References

- 1 T. Karaki, K. Yan, T. Miyamoto, and M. Adachi, Jap. J. Appl. Phys. **46**, 97 (2007).
- 2 G. Arlt, D. Hennings, and G. de With, J. Appl. Phys. **58**, 1619 (1985).
- 3 J. Yamamatsu, N. Kawano, T. Arashi, A. Sato, Y. Nakano, and T. Nomura, J. Power Sources **60**, 199 (1996).
- 4 Y. Choi, T. Hoshina, H. Takeda, and T. Tsurumi, Jap. J. Appl. Phys. **50**, 031504 (2011).
- 5 N. Halder, D. Chattopadhyay, A. Das Sharma, D. Saha, A. Sen, and H. S. Maiti, Mater. Res. Bull. **36**, 905 (2001).
- 6 T. Yonezawa, S. Takeoka, H. Kishi and K. Ida, and M. Tomonari, Nanotechnol. **19**, 145706 (2008).

- 7 S. Wang and G. O. Dayton, *J Am Ceram Soc* **82**, 2677 (1999).
- 8 A. Polotai, K. Breece, E. Dickey, C. Randall, and A. Ragulya, *J Am Ceram Soc* **88**, 3008 (2005).
- 9 Y. Choi, T. Hoshina, H. Takeda, T. Teranishi, and T. Tsurumi, *Appl. Phys. Lett.* **97**, 212907 (2010).
- 10 D. I. Woodward, I. M. Reaney, G. Y. Yang, E. C. Dickey, and C. A. Randall, *Appl. Phys. Lett.* **84**, 4650 (2004).
- 11 R. Levi and Y. Tsur, *Adv. Mater.* **17**, 1606 (2005).
- 12 Spark plasma sintering utilizes pulsed high DC current along with uniaxial pressure in a low-pressure chamber to consolidate powders. Resistive heating within the samples due to the high DC current provides the necessary temperatures for green body densification. The SPS process allows for high densification at low sintering temperatures with very high heating rates.¹³
- 13 Z. Munir, U. Anselmi-Tamburini, and M. Ohyanagi, *J. Mater. Sci.* **41**, 763 (2006).