

Nano Zirconia-Doped Barium Titanate Precursor for High Capacitance MLCC Applications

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To continue to increase the capacitance density of temperature stable MLCC devices further reduction in dielectric thickness is required. This reduction in dielectric thickness demands an improved precursor barium titanate that contributes to lower leakage currents and better degradation behavior. Hydrothermal synthesis was used to produce Zr doped BaTiO₃ powders with the composition BaTi_{1-x}Zr_xO₃ where $x = 0.0, 0.01, 0.03, 0.05, 0.10$. These powders were spherical and monodisperse from 50-150 nm in size. Lattice volume and XRF measurements confirmed the chemical composition accuracy. XRD measurements showed the influence of Zr addition on the BaTiO₃ local structure.

Key words: Barium titanate, MLCC, Nano size, Dopants, Reduction resistance

1. INTRODUCTION

The continuing evolution in the functionality of electronic devices has placed an emphasis on the miniaturization of passive components, and in particular multilayer ceramic capacitors (MLCC). This size reduction trend has resulted in much higher capacitance densities, accomplished through the use of thinner dielectric layers and stacking more dielectric layers in each component.

The reduction in dielectric layer thickness to achieve these capacitance densities necessitates the use of fine-grained ceramics with superior reduction resistance, lower leakage currents and improved degradation behavior. This improvement in reliability cannot however come at the expense of a reduction in dielectric permittivity.

These competing requirements have led to the development of dielectrics for Ni-MLCC applications utilizing a dielectric thickness of 1 μm and below¹⁻². In addition to employing rare earth dopants and codoping with transition B-site metal cations, Ca doping has been practiced to control reduction and chemical degradation. CaTiO₃ forms a solid solution with BaTiO₃ and Ca has been shown to occupy both Ba and Ti sites³. Ca doping increases the enthalpy for reduction, thereby limiting the concentration of oxygen vacancies⁴⁻⁵.

More recently Zr doping of BaTiO₃ has been investigated as an alternative to Ca⁶. In this work Zr was shown to be more effective than Ca at low concentrations in increasing band-gap energy, reduction resistance and degradation resistance without compromising dielectric permittivity or leakage current behavior.

To recognize the benefit of Ca or Zr doping of BaTiO₃ for Ni-MLCC applications it is desirable to synthesize a nano-scale powder that will result in a homogeneous, uniformly doped BaTiO₃ grain with rare earth doping at the grain boundary.

In this work the hydrothermal synthesis method was employed to produce Zr doped BaTiO₃ powders with the

composition BaTi_{1-x}Zr_xO₃ where $x = 0.0, 0.01, 0.03, 0.05, 0.10$. Two different average particle sizes were targeted, 50 nm and 150 nm to evaluate the size effect on the characteristics of the doped powders.

2. POWDER SYNTHESIS

Zr doped BaTiO₃ powders (BTZ) were synthesized by a hydrothermal process using Ba(OH)₂, TiCl₄, and ZrCl₂. The Ti and Zr containing solutions were pre-reacted prior to introduction with the Ba(OH)₂ and initiation of the hydrothermal reaction. A flow chart of the process is provided below in schematic form:

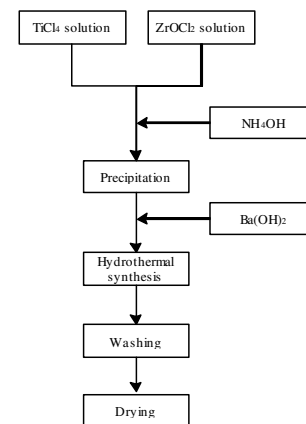


Figure 1. Hydrothermal process.

Precise control of temperature, pressure and time in the reaction vessel resulted in powders with the desired chemical composition and 50 nm particle sizes. To achieve the 150 nm particle size the powders were heat treated at 950 °C after the washing and drying step in the process.

3. RESULTS AND DISCUSSION

Following hydrothermal synthesis the BTZ powders were characterized for composition control, crystallinity, particle size and shape, moisture content, loss on ignition and impurities using XRF, XRD, DTA/TGA, SEM and TEM analytical techniques.

Table I below shows the semi-quantitative XRF analysis results for the (5) BTZ powder samples to an accuracy of ± 0.001 . The Ba, Ti and Zr contents are expressed as oxides. The relative ratios are in good agreement with the target Zr dopant levels.

Table I. Semi-quantitative XRF analysis

Sample	BTZ-9901	BTZ-9703	BTZ-9505	BTZ-9010
Batch no.	H0611024	H0610021	H0610022	H0611023
ZrO ₂ wt%	0.398	1.099	2.237	4.260
TiO ₂ wt%	32.970	32.790	31.680	29.060
BaO wt%	65.870	65.390	65.400	65.900

The BaTiO₃ - BaZrO₃ system forms a complete solid solution and follows Vegard's law, which holds that a linear relationship, at a constant temperature, exists for the lattice parameters of the composition⁷.

Figure 2 plots the measured lattice volumes for the BTZ samples synthesized in this work, both the 50 nm and 150 nm groups. The measured values are in good agreement with the fitting curve as calculated using Vegard's law.

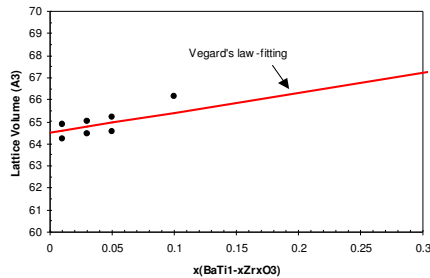


Figure 2. Lattice volume as a function of composition for BTZ powder samples.

Surface area along with SEM and TEM were used to characterize the size and morphology of the BTZ powders. Table II below summarizes the BET surface area measurements. In addition moisture content, measured as weight loss after 2 hrs. @ 105 °C and ignition loss after 1 hr. @ 1100 °C are provided. The Sr content of the BTZ powders is a function of the precursor Ba(OH)₂ raw material and is a constant 0.018 wt%.

Table II. Physical and chemical properties

Sample	BTZ-9901	BTZ-9703	BTZ-9505	BTZ-9010	BTZ-9901	BTZ-9703	BTZ-9505
Batch no.	H0611024	H0610021	H0610022	H0611023	M0625024	M0623021	M0623022
BET m ² /g	22.32	18.49	17.99	20.48	7.36	8.15	7.45
ZrO ₂ wt%	0.398	1.099	2.237	4.260	0.398	1.099	2.237
Moisture, wt%	0.49	0.51	0.5	0.48	0.47	0.49	0.46
LOI, wt %	3.38	3.4	3.36	3.36	3.35	3.4	3.38
Sr, wt%	0.018	0.018	0.018	0.018	0.018	0.018	0.018

The powders are uniformly spherical in shape and

relatively mono-disperse. Figures 3a and 3b show a SEM and TEM image for the 5 mol% BTZ sample at the 7.45 m²/g surface area.

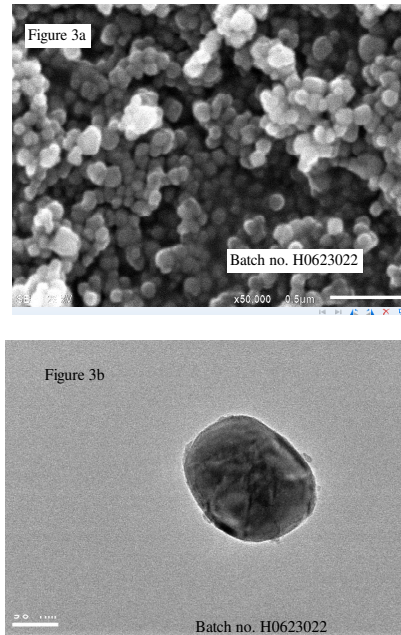


Figure 3. Micrographs of BZT-9505 by SEM (a) and TEM (b).

Figure 4 shows the systematic variation in the XRD patterns as a function of the BTZ composition. As the amount of Zr dopant increases the 2θ peak positions shift lower and tetragonality is suppressed. This behavior is consistent with local structural measurements performed on BaTi_{1-x}Zr_xO₃ solid solutions with dilute compositions⁸.

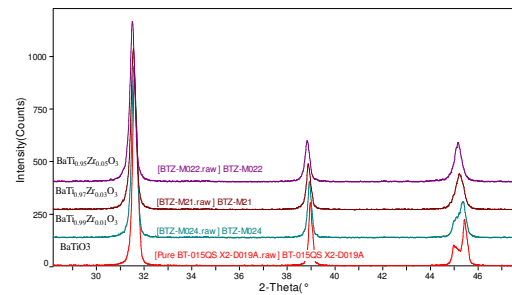


Figure 4. XRD patterns of BaTi_{1-x}Zr_xO₃ where x = 0.0, 0.01, 0.03, 0.05.

CONCLUSIONS

A series of compositions in the BaTiO₃ - BaZrO₃ system were synthesized using a hydrothermal process. These compositions were selected based on recent research that has shown dilute amounts of Zr dopant can significantly improve the reduction resistance and degradation behavior in Ni-MLCC. To promote utility in this application the BTZ powders must be nano-sized with a uniform dopant distribution.

Two target particle sizes were selected, 50 nm and 150 nm. The 150 nm particle size was achieved by employing a heat treatment at 950 °C. Surface area measurements and SEM and TEM analysis confirmed the synthesized powders were within the target particle size range. The powders were uniformly spherical in morphology and monodisperse.

Compositional accuracy was ascertained by semi-quantitative XRF analysis as well as lattice volume measurements. The XRF measurements were performed to within a ± 0.001 accuracy. The lattice volume measurements were compared to a Vegard's law curve fit and found to be in good agreement.

Structural measurements were performed using x-ray diffraction analysis. The XRD patterns showed a shift to lower 2θ values as Zr content was increased. The shift contributed to a suppression in the tetragonality of the BTZ powder.

In summary this work has demonstrated that hydrothermal synthesis is suitable for the fabrication of nano-sized, doped barium titanate powders for Ni-MLCC applications. The powders met all of the physical and chemical property design targets selected at the beginning of the study. Future work will focus on characterizing the crystal density of the powders and their temperature dependent behavior. Microstructure evolution and verification of the reduction resistance and leakage current behavior improvement will be studied in thin dielectric layers.

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