journal

J. Am. Ceram. Soc., **91** [11] 3590–3592 (2008)
DOI: 10.1111/j.1551-2916.2008.02693.x

Dielectric Constant of Barium Titanate Powders Near Curie Temperature

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Impedance spectroscopy is an effective method to investigate the dielectric properties of powders by dispersing particles in proper liquids. It allows reliable calculation of the dielectric constant by analysis of impedance spectra for a variety of particulate materials. The temperature dependence of the dielectric constant near the Curie temperature was investigated for hydrothermal barium titanate powders suspended in ethylene glycol or butoxyethanol. Room-temperature measurements revealed that the dielectric constant of hydrothermal $BaTiO_3$ powders was $\varepsilon \sim 500$. After annealing of powders at 1250°C for 1 h, the dielectric constant increased to $\varepsilon \sim 3000$. The temperature dependence of the impedance spectra was determined by conducting measurements within the temperature range from 20° to 150°C. It was shown that hydrothermal $BaTiO_3$ powders with a primarily cubic crystal structure had a suppressed temperature dependence of the dielectric constant near the Curie temperature. The dielectric constant of annealed powders with a tetragonal crystal structure was significantly higher at the Curie temperature similar to the values obtained for sintered bulk barium titanate.

I. Introduction

Because the dielectric properties of particulate materials may significantly differ from that of bulk materials, dielectric characterization of powders requires the development of reliable and reproducible measurement techniques. A new approach for dielectric powder characterization was introduced in our previous publications.[1–3] This approach is based on application of impedance spectroscopy techniques to the slurries of dielectric powders and extracting the information on the dielectric properties of the particles from the low-frequency part of the spectra. It was shown that the low-frequency part of the impedance spectra contains valuable information on the dielectric properties of dispersed particles, which can be extracted from the low-frequency semicircle in a relatively simple way. These studies showed that impedance spectroscopy techniques allow accurate and reliable measurement of the dielectric constant of particles ($\varepsilon \sim 100$–2000) suspended in host liquids ($\varepsilon \sim 10$–65). To evaluate the validity of the developed method, dense $BaTiO_3$ cubes, of $\sim 1\ mm^3$ size, were used as model samples to prepare suspensions instead of using powders. The dielectric constant of model samples was found to be identical to that of the bulk samples.[3] Application of this method to determine the dielectric constant of particles by impedance spectroscopy techniques and interpretation of the results by equivalent circuit models was confirmed by Nakao[4] in a follow-on study.

The use of nanometer-sized powders plays an important role in development of dielectric materials. Unlike micrometer-sized powders, the dielectric properties of nanoparticles can vary depending on the powder synthesis methods and heat-treatment conditions. Different experimental techniques can be used for direct or indirect characterization of the dielectric behavior of powders with various average particle sizes. Direct measurements of the dielectric constant of nanoparticles usually use dispersion of the powders in a host liquid and extraction of the powder's dielectric constant from high-frequency electrical data of 0–3 type systems.[5–10] Unfortunately, these approaches use one of the effective medium formulas to extract the dielectric constants of powders and do not allow confirmation of the correctness of the calculated values.

Barium titanate exhibits several ferroelectric phase transitions in the low-temperature range including a tetragonal–cubic transition at $\sim$120°C. Various methods can be used to investigate these anomalies and to make indirect conclusions with regard to the value of the dielectric constant of particles as a function of temperature. Differential scanning calorimetry (DSA), Raman spectroscopy, and X-ray diffraction (XRD) can be mentioned as examples of such approaches.[11–13]

It is well known that barium titanate exhibits a tetragonal/cubic phase transition near 120°C, which causes significant anomaly of the dielectric constant. It seems possible to use the slurry approach combined with impedance spectroscopy measurements to investigate this anomaly for $BaTiO_3$ powders. Because the Curie temperature of the corresponding phase transition in $BaTiO_3$ is lower than the boiling point of host liquids, temperatures as high as 150°C can be applied to the slurries below the boiling temperature of the host liquid such as ethylene glycol or butoxyethanol.

The objectives of this study are: (i) to show the applicability of impedance spectroscopy in order to determine the dielectric constant of barium titanate powders within an extended temperature range, (ii) to measure the real anomalies in the dielectric constant of powdered barium titanate, and (iii) to correlate the intensity of these anomalies with the crystal structure of barium titanate particles.

II. Experimental Procedure

Hydrothermally synthesized $BaTiO_3$ powders (TPL Inc., Albuquerque, NM) before and after annealing at 1250°C for 1 h were used in this study. The powder had an average particle size of $\sim$0.3 μm and became agglomerated after annealing at 1250°C. The crystal structure and phase transformation of the powders were characterized by (XRD) and differential scanning calorimetry techniques, respectively. Slurries were prepared using ethylene glycol (99.8%, $\varepsilon = 37$, Sigma-Aldrich, Milwaukie, WI) and butoxyethanol (>99%, $\varepsilon = 10$, Fisher Scientific, Houston, TX) by dispersing powders ultrasonically for 10 min in the host liquids.

An electrochemical cell with stainless-steel electrodes (surface area 4 cm^2, distance between the electrodes: 0.15 mm) was assembled as a sample holder for electrical characterization of

C. A. Randall—contributing editor

Manuscript No. 24356. Received February 27, 2008; approved August 7, 2008.
This work was supported by the National Science Foundation, as part of the Center for Dielectric Studies under Grant No. RG001083 and through a MURI program sponsored by the Office of Naval Research under Grant No. N000-14-05-1-0541.
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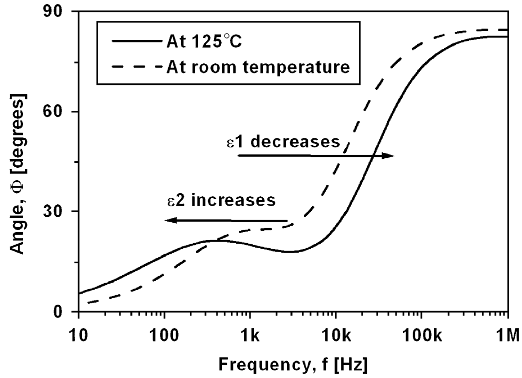

Fig. 1. Phase angle as a function of frequency measured using a butoxyethanol-based slurry with 20 vol% $BaTiO_3$ powder before annealing. Dielectric constant measurements were conducted at room temperature (dashed line) and at 115°C (solid line).

the slurries. For temperature-dependent measurements, the sample holder was immersed into a beaker filled with the host liquid (butoxyethanol or ethylene glycol), which was temperature controlled on a hot plate. The temperature of the slurry was monitored using a thermocouple attached to the sample holder. An automated Solartron system (1255b Frequency Response Analyzer and 1470 Cell Tester, Farnborough, Hampshire, U.K.) was used to collect the data of the impedance spectra.

III. Results and Discussion

The temperature dependence of the dielectric constant of hydrothermal $BaTiO_3$ powders was studied by conducting impedance spectroscopy measurements using slurries within the temperature range from 20° to 150°C. Figure 1 shows the effect of temperature on the impedance spectra, i.e. frequency dependence of the phase angle, obtained using slurries prepared from "as-received" powders. The impedance spectra revealed two distinct features: (i) high-frequency relaxation defined mostly by the dielectric constant of the host liquid (ε_1) and (ii) low-frequency relaxation defined mostly by the dielectric constant of the particles (ε_2) in the slurry. There is a distinct difference between the two spectra obtained by measurements from 20°C to near the Curie temperature $\sim$125°C. High-frequency relaxation shifts to higher frequencies due to the decrease of the dielectric constant of butoxyethanol from $\sim$10 at room temperature to $\sim$8 at 125°C. Low-frequency relaxation shifts to lower frequencies, which indicates an increase of the dielectric constant of particles near the Curie temperature, i.e. the presence of ferroelectric behavior.

The temperature dependence of the dielectric constant of particles calculated from low-frequency relaxation of the impedance spectra is shown in Fig. 2. The powders were dispersed in two different liquids: ethylene glycol and butoxyethanol. Nearly the

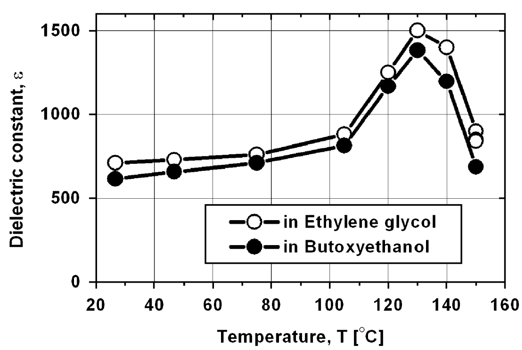

Fig. 2. Temperature dependence of the dielectric constant of hydrothermal $BaTiO_3$ powder before annealing measured using 20 vol% slurries of ethylene glycol and butoxyethanol as dispersion media.

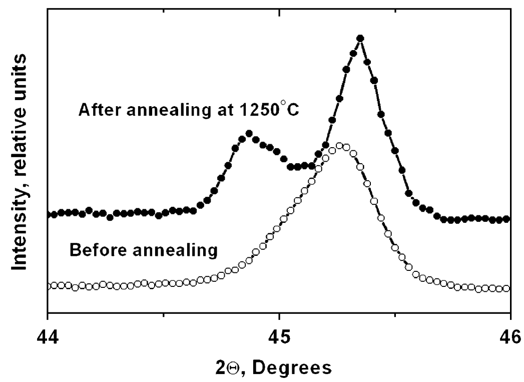

Fig. 3. X-ray diffraction pattern of hydrothermal powders before (open circles) and after (closed circles) annealing at 1250°C.

same values of the dielectric constant of particles were measured for slurries prepared using both liquids over the given temperature range. This indicates that the measured values are correlated with the dielectric properties of particles in the slurry.

It is well known that the crystal structure of hydrothermally prepared $BaTiO_3$ is predominantly cubic, which is generally attributed to the presence of hydroxyl ions incorporated within the particles. Such powders exhibit low dielectric constant values within a broad temperature range including Curie temperature. Annealing of powders at an elevated temperature results in an increase of tetragonality of powders. XRD patterns of powders before and after annealing are shown in Fig. 3. It is revealed that the powders before the annealing consist mainly of a cubic crystal structure as indicated by a slightly distorted single peak.

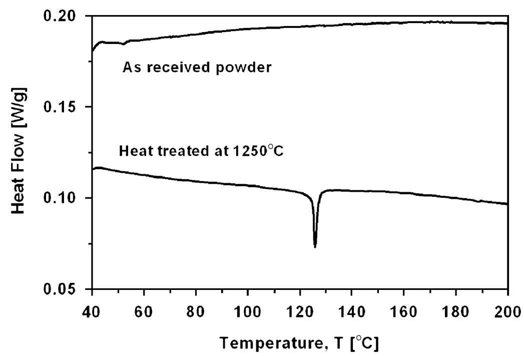

Fig. 4. Differential scanning calorimetry results of hydrothermal powders before and after annealing at 1250°C. Annealed powder shows the cubic–tetragonal phase transformation at the Curie temperature $\sim$125°C.

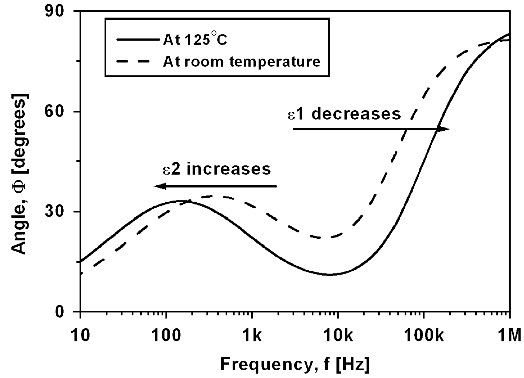

Fig. 5. Phase angle as a function of frequency measured using slurries prepared with butoxyethanol and 20 vol% barium titanate powder annealed at 1250°C. Data obtained at room temperature (dashed line) and at 115°C (solid line).

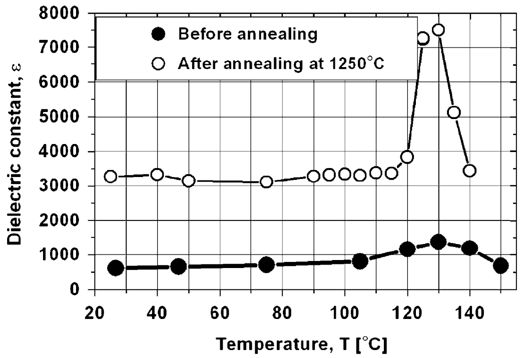

Fig. 6. Temperature dependence of dielectric constant for hydrothermal $BaTiO_3$ powders before and after annealing at 1250°C. Slurries were prepared using butoxyethanol with solids loading of 20 vol%.

After annealing at 1250°C, the crystal structure of agglomerated powders is tetragonal and shows splitting of the peak near $2\theta = 45°$. Figure 4 shows the results of the heat flow as a function of temperature obtained through characterization of the powders using DSC. These results confirm the Curie temperature of annealed powders at ~125°C and the absence of a cubic–tetragonal phase transformation for the hydrothermal $BaTiO_3$ powders before annealing.

Impedance spectra of slurries with annealed powders measured at room temperature and 125°C are shown in Fig. 5. Both spectra appear similar to that of the initial powder in Fig. 1. High-frequency relaxation was affected primarily by the dielectric constant of the host liquid (ε_1) while low-frequency relaxation was affected primarily by the dielectric constant of dispersed powder (ε_2). High-frequency relaxation shifts to higher frequencies due to a decrease of the dielectric constant of butoxyethanol at elevated temperatures (from ~10 at room temperature to ~8 at 125°C). Low-frequency relaxation shifts to even lower frequencies, which indicates an increase of the dielectric constant near the Curie temperature or the presence of ferroelectric behavior. At the same time, the frequency gap between low- and high-frequency relaxations increases in case of annealed powders, indicating an increase of the dielectric constant of particles. The temperature-induced shift of low-frequency relaxation becomes more significant, indicating an increase of the dielectric constant near the Curie temperature.

Even a relatively small amount of the tetragonal phase present in hydrothermal powders can give rise to an increase of the dielectric constant at the Curie temperature as shown in Fig. 6. It is revealed that the dielectric constant of hydrothermal powders primarily with a cubic crystal structure is low ($\varepsilon \sim 500$), as expected, and increases slightly at the Curie temperature, which indicates the presence of a small fraction of the tetragonal phase. After annealing at 1250°C, the dielectric constant of powders with a tetragonal crystal structure increases significantly ($\varepsilon \sim 3000$) and shows a strong anomaly at the Curie temperature ($\varepsilon \sim 7000$) similar to that observed for sintered bulk $BaTiO_3$.

IV. Summary

The temperature dependence of the dielectric constant of barium titanate powders was determined by impedance spectroscopy techniques. Hydrothermally prepared powders before and after annealing at 1250°C for 1 h were used for preparation of slurries with 20 vol% solids loading in butoxyethanol. The dielectric constant of powders before annealing was rather low ($\varepsilon \sim 500$) and revealed a slight increase at the Curie temperature, which is attributed to the presence of a small fraction of the tetragonal phase in powders with a primarily cubic crystal structure. The dielectric constant of annealed powders with a tetragonal crystal structure increased ($\varepsilon \sim 3000$) and showed a strong anomaly ($\varepsilon \sim 7000$) at the Curie temperature.

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