

DIELECTRIC BEHAVIOUR OF BaTiO₃ PREPARED BY SOL-GEL TECHNIQUE WHEN EXPOSED TO DIFFERENT OXYGEN CONCENTRATIONS

YEOH CHEOW KEAT¹, SRIMALA SREEKANTAN², SABAR DERITA HUTAGALUNG³ & ZAINAL ARIFIN AHMAD⁴

Abstract. The dielectric properties of BaTiO₃ powders prepared by a low temperature aqueous route when exposed to different oxygen concentrations have been studied by means of impedance spectroscopy. Due to the differences of solubility of Ba and Ti in aqueous solutions, deviations from stoichiometric ratios (a 10% excess) and higher solution pH (pH~13) were necessary. XRD traces and TG-DTA curves show the formation of nearly phase-pure BaTiO₃ with higher calcinations temperatures promoting greater crystallinities. Dielectric measurements using impedance spectroscopy show the samples to consist of more than one electrical element including a low resistivity core, a high capacitance grain boundary and a ferroelectric bulk component. Exposing the samples to different oxygen concentrations caused a slight increase in resistivities with increasing oxygen concentration, which was attributed to the oxygen stoichiometry. A greater increase in the capacitance of the grain boundary component was also observed compared to the ferroelectric bulk.

Key words: Sol-gel processes, chemical processes, dielectric properties, BaTiO₃.

Abstrak. Sifat dielektrik serbuk BaTiO₃ yang disediakan melalui kaedah akues pada suhu rendah telah dikaji menggunakan kaedah spektroskopi impedans apabila didedahkan terhadap tahap oksigen yang berbeza. Untuk mengatasi masalah kebolehlarutan Ba dan Ti yang berbeza, nisbah sebatian Ba yang ditambah lebih tinggi daripada nisbah stoikiometri (tambahan 10%) dan nilai pH larutan yang tinggi (pH~13) diperlukan. Ujian XRD dan TG-DTA menunjukkan BaTiO₃ yang hampir tulen dapat disintesis melalui kaedah ini. Suhu pengkalsinan yang lebih tinggi menghasilkan darjah penghabluran bahan yang lebih tinggi. Kajian dielektrik menunjukkan bahan yang dihasilkan mengandungi lebih daripada satu elemen keelektrikan antaranya teras berkerintangan rendah, sempadan butiran berkapasitan tinggi dan suatu elemen pukal feroelektrik. Setelah didedahkan terhadap tahap oksigen yang lebih tinggi, nilai kerintangan sampel bertambah, yang mungkin disebabkan stoikiometri oksigen pada sampel yang diuji. Peningkatan dalam nilai kapasitan daripada sempadan butiran adalah lebih ketara jika dibandingkan dengan peningkatan unsur feroelektrik pukal.

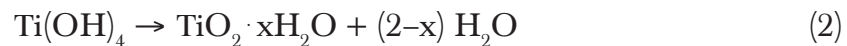
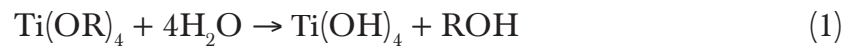
Kata kunci: Kaedah sol-gel, sintesis kimia, sifat dielektrik, BaTiO₃

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1.0 INTRODUCTION

This paper studies the dielectric properties of barium titanate pellets prepared through a sol-gel technique, when exposed to different oxygen concentrations in a reducing atmosphere. Wet chemical synthesis [1–3] holds several advantages over conventional solid state methods including lower processing temperatures, lesser risk of contamination by grinding media as well as very fine grain sizes. In addition, the solution form is suitable for the synthesis of thin films through spin coating, dipping or even ink-jet printing [4–6].

Low temperature aqueous synthesis usually starts from the preparation of a TiO_2 sol prepared from the hydrolysis and subsequent peptization of the titanium alkoxides.



Barium ions in the form of soluble salts are then added to the solution. The potential-pH diagram [7] (Figure 1) shows that the Ti species is soluble in aqueous solutions at $\text{pH} < 3$, while Ba ions are soluble over a wide range of $\text{pH} < 13$. The differences in solubility cause the leaching of Ba ions from BaTiO_3 particles suspended in aqueous solutions leaving a TiO_2 skin on the particles [1, 8]. Increasing the pH value of the solution to pH 13 causes the precipitation of BaTiO_3 because it is the only stable phase under these conditions.

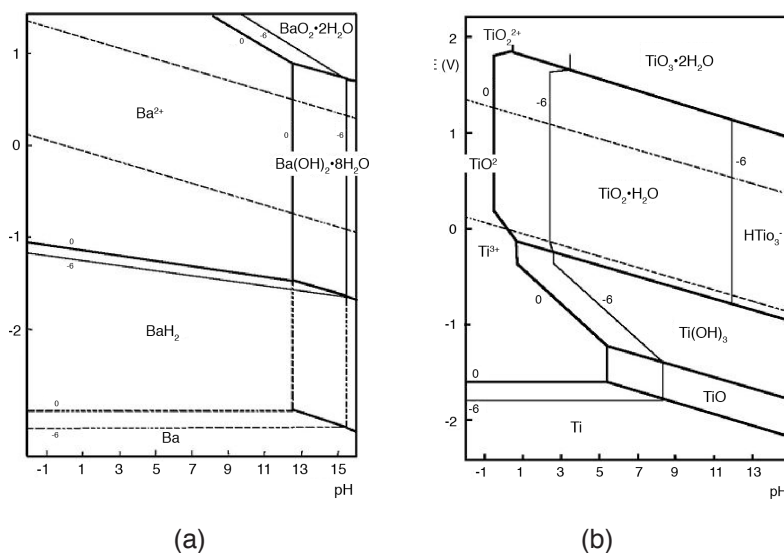


Figure 1 Potential-pH diagram for (a) Ba and (b) Ti in aqueous solutions (after Pourbaix, 1966)

Two mechanisms are widely agreed upon to be possible for the formation of the BaTiO₃ from the aqueous solution. In-situ transformation or diffusion dominant processes involve the reaction of Ba ions with the TiO₂ particle to form a BaTiO₃ shell around the particle with process continuation dependent on the diffusion of Ba ions through to the TiO₂ core. The dissolution-precipitation mechanism involves the dissolution of TiO₂ into a Ti(OH)_x^{4-x} species before precipitation by reaction with barium ions. It has been suggested that dissolution-precipitation dominates at the initial stages while the diffusion dominant processes are more important during the later stages of particle growth.

Impedance spectroscopy is a method for measuring the frequency response of a material to an alternating current. Since ceramics are, by nature, electrically heterogeneous, this technique makes it possible to differentiate between the different electrical elements.

2.0 MATERIALS AND METHODS

0.4 M titania sol was prepared via the hydrolysis of tetrabutyl orthotitanate [Ti(C₄H₉O)₄; Fluka] and subsequent peptization using nitric acid [HNO₃; Fluka]. Ti(C₄H₉O)₄ was diluted using butanol [C₄H₉OH; Fluka] and added dropwise into a water-butanol mixture under vigorous stirring. Appropriate amounts of barium chloride dihydrate [BaCl₂·2H₂O; Fluka], dissolved in deionized water to form 0.4 M resistances were corrected by the sample geometry as well as measured ohmic drop for each measurement condition.

3.0 RESULTS AND DISCUSSION

The TG-DTA curves for the bulk powders (Figure 2) up to 1000°C show the presence of a broad exothermic peak below 200°C with a corresponding drop in the TG curve. This might be attributed to the decomposition of organics and drying of the precipitates. No further peaks were observed beyond 800°C which might suggest that no further phase changes occurred beyond this threshold.

A weight loss at 600°C was observed for all the samples, which might be attributed to the decomposition of some residual BaTiO₂CO₃ into the final BaTiO₃ phase [10];



or in the case of complete formation of the intermediate compound,



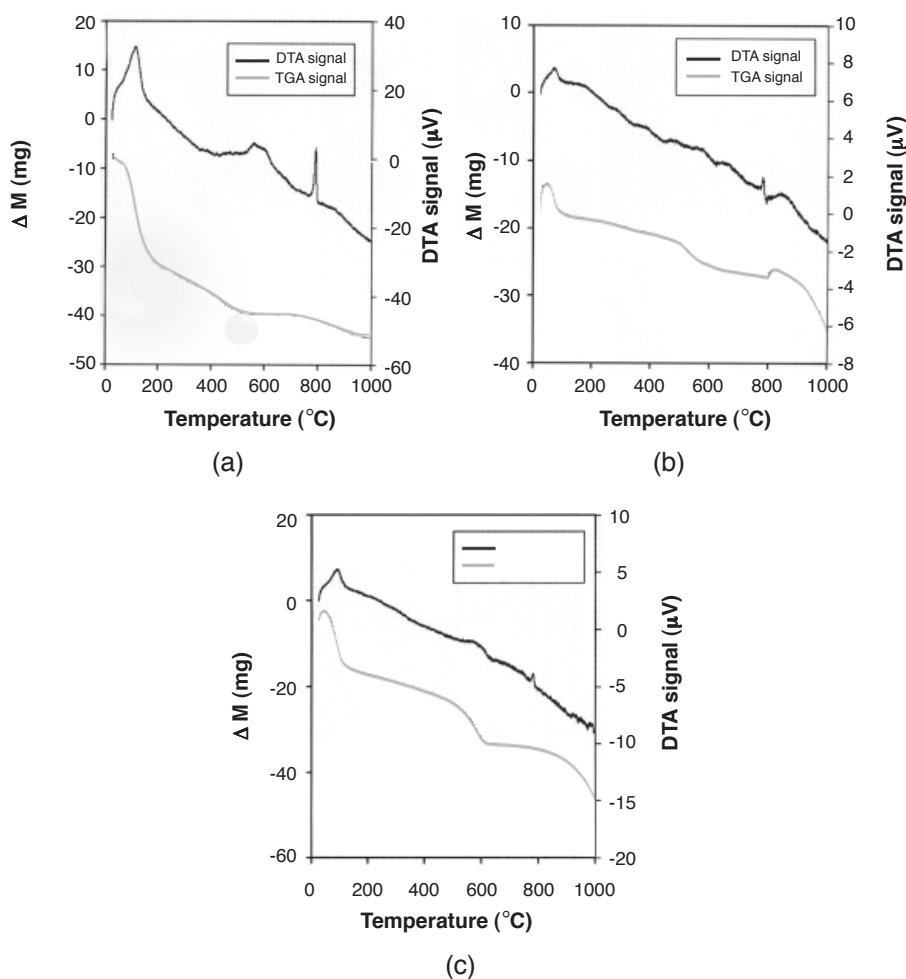


Figure 2 TG-DTA traces for samples prepared using (a) stoichiometric additions of Ba ions at pH 1, (b) Ba ion additions in stoichiometric ratios at pH 13, and (c) Ba ion additions 10 % in excess of the stoichiometric ratio at pH 13

Although the sealed bottles were purged with Ar to remove atmospheric CO_2 , it is not impossible that some CO_2 diffused during separation of the precipitates or during drying. These reactions were preferred over the decomposition of BaCO_3 as the solutions were purged with Ar to remove atmospheric CO_2 and, due to the leaching of Ba ions from the BaTiO_3 particles, precipitates from solutions $\text{pH} < 13$ were Ba-deficient. The presence of BaTiO_3 in the XRD patterns (Figure 3) of the as-dried precipitates might indicate that insufficient CO_2 was obtained from atmosphere during drying for complete formation of $\text{BaTiO}_2\text{CO}_3$ which inhibits the crystallization of BaTiO_3 below 600°C .

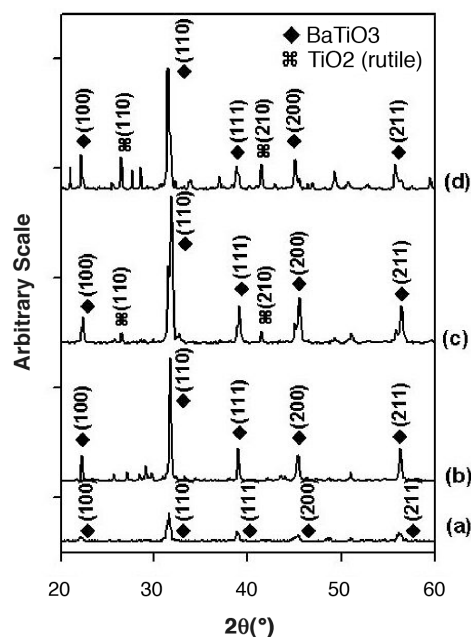


Figure 3 XRD traces of (a) as precipitated samples prepared with an extra 10% Ba ion addition as well as calcined samples prepared with (b) an extra 10% Ba ion addition at pH 13, (c) stoichiometric additions of Ba ions at pH 13, and (d) stoichiometric additions of Ba ions at pH 1

A small exothermic peak was observed at 800°C which did not have a corresponding weight change. This might be due to a structural change such as the anatase to rutile conversion. The height of this peak was observed to decrease with decreasing amounts of TiO₂ as observed in the XRD traces which further strengthens the possibility of these peaks being due to the anatase-rutile conversion. This is in agreement with the previous findings whereby the Ba was more soluble than the Ti[1]. Several authors have observed this phenomenon and, attributing the loss to the dissolution of Ba ions during the washing, compensated by adding Ba salts in excess of the stoichiometric ratio to counteract the effects of this leaching. This was observed in spite of the pH being adjusted to a high pH > 13, and was not entirely unexpected as even the potential-pH diagram [7] was built around the limits of detection for the ion solubility.

XRD traces (Figure 3) of the bulk powders show that the powders prepared with pH values 1 through 11 and/or stoichiometric or less than stoichiometric Ba ion additions resulted in extra TiO₂ peaks (Figure 3c and 3d) while powders prepared with a 10 wt% excess of Ba at pH 13 were single phase BaTiO₃ without

the presence of detectable excess TiO_2 . A stoichiometric ratio is important because excess Ba might lead to the formation of Ba_2TiO_4 which inhibits grain growth while excess Ti might cause the formation of a liquid phase eutectic during sintering [11].

The brick model separates most ceramics into insulating grains and the semiconducting grain boundaries. The equivalent circuit for this is usually represented by two parallel resistor-capacitor (RC) elements connected in series [1, 12] to account for the bulk and grain boundary contributions respectively. The impedance data was reported in the impedance complex plane (Figure 4a) and in modulus spectroscopic form (Figure 4(b)) with electric modulus, M^* calculated from the relation

$$M^* = j\omega C_0 Z^* \tag{6}$$

where $j = \sqrt{-1}$, C_0 represents the vacuum capacitance of a cell with similar geometry to the sample and $\omega = 2\pi f$ with f representing the frequency in Hz. M^* and Z^* represent the real and imaginary components of the electric modulus and impedance respectively.

$$M^* = M' - jM'' \tag{7}$$

$$Z^* = Z' - jZ'' \tag{8}$$

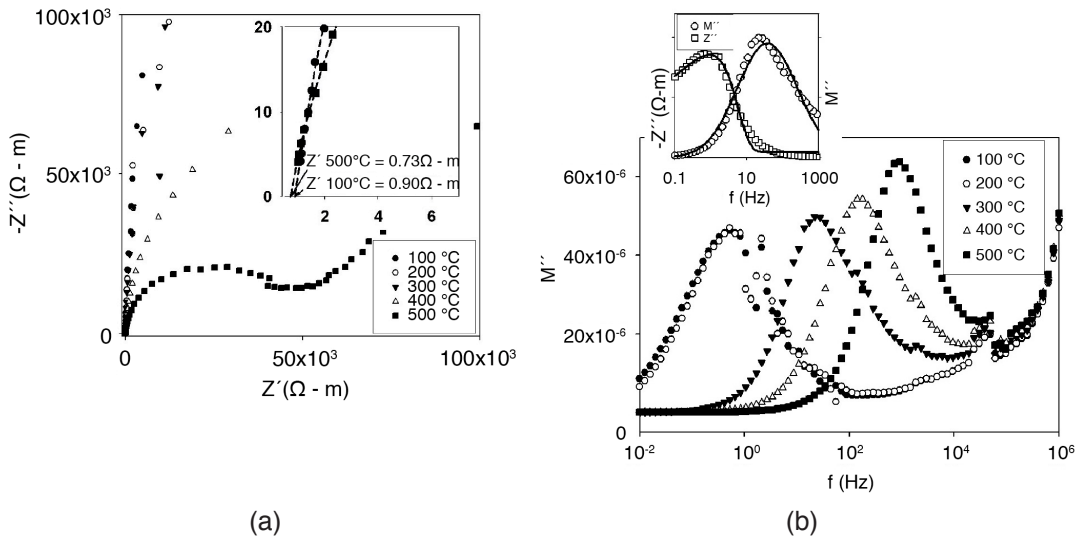


Figure 4 The (a) impedance complex plane and (b) electric modulus formalism representations of the BaTiO_3 samples heated to different temperatures. The insets for 4(a) and 4(b) show the non-zero intercepts and the non-coinciding Z'' and M'' peaks respectively

Each RC element typically results in a hemisphere in the complex plane representations with overlapping arcs sometimes resulting in conjoined arcs or deformed hemispheres. The spectroscopic electric modulus representations give a clearer view of the different regions than impedance representations, especially when overlapping arcs are present [13]. In addition, the grain-boundary and bulk (as estimated by the non-zero intercept of the complex plane impedance arc) components was plotted in the Arrhenius form,

$$\sigma = \sigma_o \exp\left(-\frac{E_a}{kT}\right) \quad (9)$$

where σ represents the reciprocal of the resistivity, σ_o the preexponential factor, E_a is the activation energy, k Boltzman's constant and T the temperature in K .

The impedance complex plane representations show decreasing arcs, indicative of decreasing resistance, with increasing temperatures (Figure 4(a)). A low frequency incline in this representation was also observed which is likely due to the diffusion influenced Warburg impedance.

The modulus spectroscopic representations (Figure 4(b)) show only a single peak for nearly all temperatures as well as a gradual increase with increasing frequency which might indicate the presence of another peak, which lay beyond the 1 MHz frequency limit used in the experiments. The full width at half maximum of the peaks were greater than 1 decade indicating broadening due to overlapping peaks caused by the presence of more than one circuit element. Superimposing the complex impedance with the electric modulus show non-coinciding peaks that further support this supposition (Figure 4(b)).

Other researchers [13] have noted the presence of several elements in the electrical microstructure including a low resistivity core, a high capacitance grain boundary, as well as a low capacitance bulk component. Three elements were assigned to the samples. The resistivity of the first element was estimated from the non-zero intercept of the complex impedance plane plot, while the resistivity and capacitance of the second and third elements were estimated from the two different peaks obtained in the spectroscopic impedance and modulus plots. The capacitance of the first element could not be estimated because no visible Debye peaks could be seen in the spectroscopic plots at these temperatures. The high resistivity of the samples < 300 °C made it difficult to obtain a complete arc and capacitance values, where necessary, were obtained by partial curve fitting.

The resistivities of the three different elements were found to approximate the Arrhenius law (Figure 5), with elements 1, 2 and 3 having activation energies, E_a , of 0.06 eV, 0.71 eV and 0.74 eV respectively. The very low resistivity values might indicate that element 1 represents the low resistivity core of the samples.

The low activation energies for elements 2 and 3 when taking into account that pure BaTiO_3 has a band gap of $\sim 3\text{eV}$ [14] indicates the presence of extrinsic factors influencing the change in resistivity, possibly due to the nitrogen environment. It is well known that heating pure barium titanate in a reducing atmosphere at elevated temperatures changes the properties from an insulator to a semiconductor [15, 16] and this was attributed to the oxygen stoichiometry of the grain boundaries and a subsequent core-shell structure.

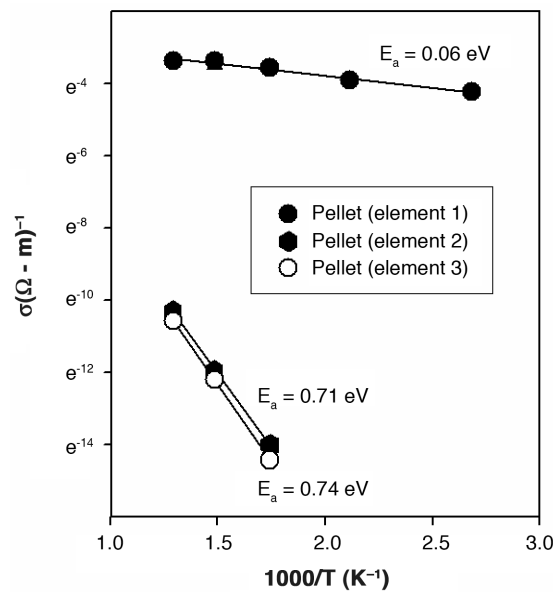


Figure 5 The reciprocal of the resistivity for the different elements represented in an Arrhenius plot

The relative permittivity of the grain boundary component, as estimated from the spectroscopic Z'' plot (not shown because of the very large change in resistance values), decreased with increasing temperature while the peaks in the electric modulus formalism (Figure 4(b)) shifted very slightly to the right. A Curie-Weiss plot (Figure 6) of the capacitances of both elements show that element 3 shows ferroelectric behaviour, with a T_c of 150°C , while element 2 does not. This reason and the relatively high capacitance value of element 2, $\sim 10^{-8}$ F·m when close to the Curie temperature, might indicate that element 2 is representative of the high capacitance grain boundary contribution while element 3 is indicative of a ferroelectric bulk contribution.

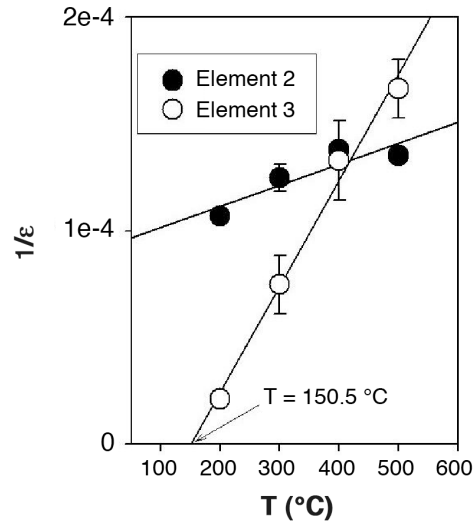


Figure 6 A Curie-Weiss plot for the samples

Figure 7 shows the change in resistivity while Figure 8 shows the change in relative permittivity when oxygen was introduced into the testing atmosphere in varying concentrations. Element 1, assigned to a low resistivity core, showed an increase in resistivity when oxygen was introduced. The permittivity of the samples increased with increasing oxygen concentration. A greater change was observed in element 2 (grain boundary) compared to element 3 (ferroelectric bulk).

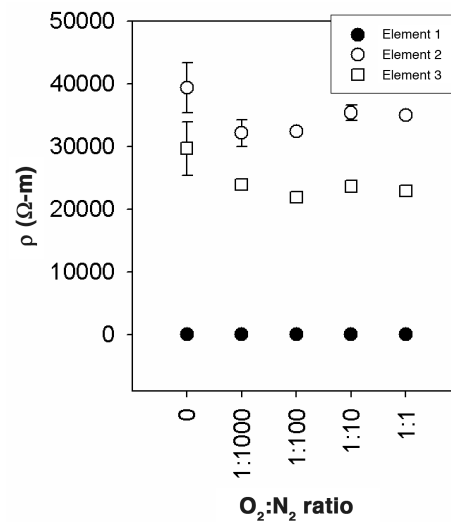


Figure 7 The change in resistivities when oxygen content was varied

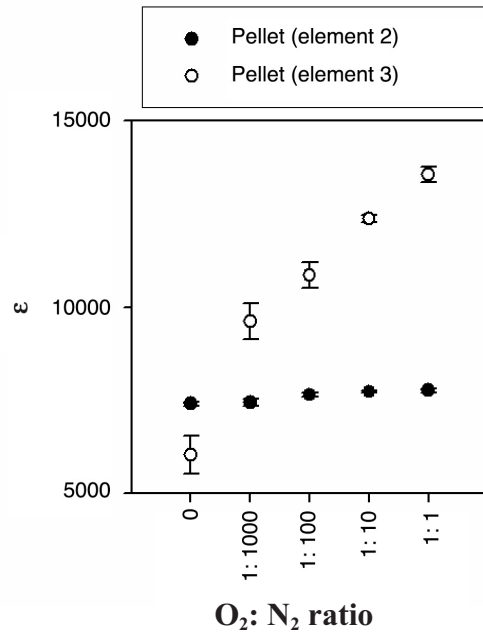


Figure 8 The change in permittivities of the pellets and thin films with oxygen content in reducing environment

4. CONCLUSIONS

BaTiO₃ powders were prepared using a low temperature aqueous synthesis. The as-precipitated powders showed lower crystallinity compared to powders calcined at 1100°C. Impedance spectroscopy show the samples to consist of several electrical elements, including a low resistivity core, a high capacitance grain boundary as well as a ferroelectric bulk component. Varying the oxygen concentration of the testing atmosphere caused the resistivities and permittivities of the grain boundary component to increase.

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