Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 34 (2008) 933–937
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Investigation of grain boundaries influence on dielectric properties in fine-grained $BaTiO_3$ ceramics without the core–shell structure

Nobuyuki Wada *, Takashi Hiramatsu, Toshiyuki Tamura, Yukio Sakabe

Murata Manufacturing Co., Ltd., 1-10-1 Higashi-koutari, Nagaokakyo-shi, Kyoto 617-8555, Japan

Available online 29 September 2007

Abstract

Grain boundaries of the Ca-doped and fine-grained $BaTiO_3$ (BT) ceramics were investigated in order to understand the role of grain boundaries, using a high-resolution transmission electron microscope (TEM) analyses, X-ray diffraction (XRD) and chemical etching analyses. Electrical properties and complex impedance spectroscopy of multilayer ceramic capacitors (MLCs) using Ca-doped BT were also examined to investigate with reference to the roles of grain boundaries. Doped elements were peculiarly enriched at the grain boundaries and tetragonality of the BT ceramics recovered significantly after grain boundaries were etched. It is confirmed that the grain boundaries have a significant influence in stabilizing the temperature dependence of the dielectric properties, and that the residual stress is caused by grain boundaries with the grain growth inhibited during sintering. In addition, the high reliability of BT ceramics without the core–shell structure is considered to be due to the high resistivity of the grain boundaries.

Keywords: B. Grain boundaries; C. Dielectric properties; D. $BaTiO_3$; E. Capacitors

1. Introduction

With development of electronic devices such as mobile phones, personal computers, and various digital electric appliances, electronic passive components have continued to become progressively smaller in size. In the case of MLCs, many works have actively improved their performance, especially with the thickness of dielectric layers becoming thinner in order to miniaturize their sizes and to have larger capacitance. These days, MLCs with 1 μm dielectric layer in thickness have already appeared on the world market and the market for large capacitance capacitors, more than 10 μF, is recently expanding and replacing that for Ta and Al electrolytic capacitors.

MLCs with large capacitance commonly consist of BT-based ferroelectric material for dielectrics and Ni-base metal for inner electrodes, so MLCs have to be fired in a reducing atmosphere to prevent Ni electrodes from oxidation. There are many kinds of dielectric materials developed for MLCs with Ni electrodes [1–3]. The core–shell BT ceramics are widely used for MLCs with the specification of X7R (EIA code: $\Delta C/C = \pm 15\%$ at −55 to 125 °C), showing a stable temperature dependence of the dielectric constant and a high reliability [4-8]. As shown in Fig. 1(a), the core part of the core–shell BT is pure BT, which is characterized as the ferroelectric phase, and the shell part, which was modified with some dopants, is the paraelectric phase or the diffused ferroelectric phase at room temperature. The temperature dependence of the dielectric constant is considered to be a combination between dielectric constants of the core and the shell part. The high reliability is considered to be due to the high reliability of the shell which controls the composition of the shell part.

Fine-grained dielectric ceramics with high dielectric constant have been required for thinner dielectric layers. However, it is well known that ferroelectric materials like BT ceramics have some degree of grain size dependence in ferroelectricity [9,10] and the dielectric constant decreases depending on the decrease of grain diameter [11]. The core–shell ceramics were considered to be especially difficult to possess high dielectric constant in very fine grain ceramics [12], because of smaller size of the core part possessing ferroelectricity. Instead of the core–shell dielectrics, alternative fine-grained BT ceramics without the core–shell structure were proposed [13,14], as shown in Fig. 1(b), and it was reported that

* Corresponding author.
E-mail address: nobuwada@murata.co.jp (N. Wada).

0272-8842/$34.00 © 2007 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2007.09.061

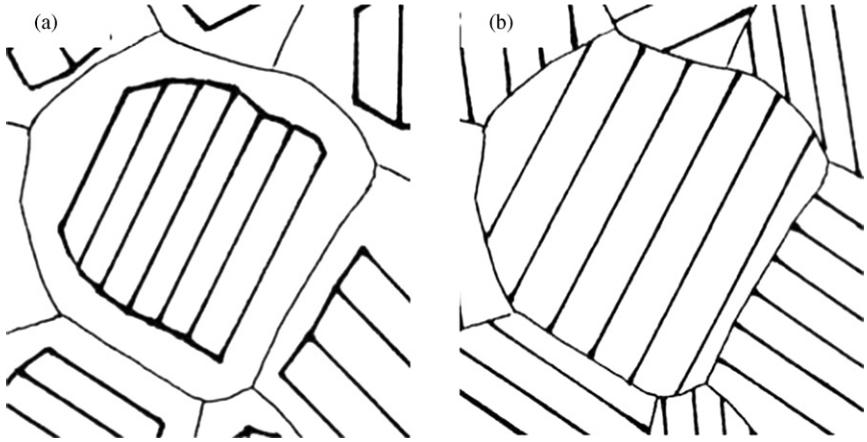

Fig. 1. Schematic diagrams of the core–shell structure (a) and the non-core–shell structure (b). Solid lines in grains mean the ferroelectric domain structure.

these newly developed fine-grained ceramics had already been applied to MLCs with 1 μm dielectric layer in thickness [15,16].

These new dielectric BT ceramics show a high dielectric constant, because grains show high ferroelectricity throughout the entire volume of the grains, and a stable temperature dependence of the dielectric constant similar to the core–shell dielectric ceramics. The reason why they have the stable temperature dependence is assumed as follows. In the BT ceramics, the grain growth is inhibited during sintering as in the core–shell ceramics. The inhibition of the grain growth results in large stress in the grains from grain boundaries and hence the maximum dielectric constant at the Curie temperature is depressed by the surface stress of grains [13]. The high reliability of the new dielectrics without the core–shell structure results from the high reliability of grain boundaries enforced with some additional elements [14].

The above shows that grain boundaries are considered to have important roles in the fine-grained ferroelectric ceramics, especially for ceramics without the core–shell structure. However, the role of grain boundary in influencing dielectric properties has not been investigated in enough detail. In this report, the influence of grain boundaries on dielectric properties in fine-grained BT ceramics without the core–shell structure was investigated.

2. Experimental procedure

The purpose of the experiments in this report is to investigate the effect of grain boundaries on dielectric properties. The authors have already reported that Ca doping to BT is very effective in improving reliability [14], so Ca-doped BT (BCT) was used as main the BT raw material in this experiment. BCT powders were prepared by a hydrolysis method using $Ba(OH)_2$, Ti alkoxide, and $CaCl_2$. Raw materials were mixed above 80 °C for 3 h in the solution to pH 12. After washing, drying and calcining at 1050 °C in air, they were then mixed with 1 mol% $MgCO_3$, 0.2 mol% $MnCO_3$, 2 mol% SiO_2, and 0.5 mol% Y_2O_3. Formulated powders were mixed with an organic binder, ethyl alcohol and toluene to prepare slurries. Ceramic green films were prepared using the doctor blade method, then stacked and pressed. Two types of samples were prepared. One was the MLCs with Ni electrodes, in which the thickness of dielectric layer was 4 μm. The other was the disc sample that was 5 mm in diameter and 0.7 mm in thickness.

Disc and MLCs samples were fired in a reducing atmosphere (1.6×10^{-11} MPa O_2 at 1150 °C or 7.2×10^{-10} MPa O_2 at 1300 °C) to control grain growth during sintering. Obtained samples without grain growth during sintering were mainly examined by the following analyses. Chemical etching analyses on disc samples were conducted in HCl dilute solution to investigate grain boundaries properties. Reacted etching solutions in etching were measured by an inductively coupled plasma-atomic emission spectrometry (ICP-AES). Etched disc ceramics were analyzed by SEM observation, TEM observation, and XRD analysis to determine the influence on the lattice distortion by the grain boundary. The lattice distortion was estimated by the Hall method [17]. The capacitance and dissipation factor of MLCs were measured at 1 kHz and 0.5 V_{rms}/μm, using a LCR meter (HP-4284A). The frequency properties of MLCs were examined from 0.01 Hz to 1 MHz with an electric field of 1 V/μm at 200 °C, using the Novocontrol BDS system to draw the complex impedance spectroscopy.

3. Results and discussion

Fig. 2 shows temperature dependences of dielectric constant of the BCT ceramics, revealing the difference between the ceramics with grain growth and without grain growth during sintering. The BCT ceramics with grain growth show typical temperature dependence of dielectric constant with a high dielectric constant at the Curie temperature. On the other hand, the ceramics without grain growth show stable temperature dependence, with the dielectric peak at the Curie temperature depressed and showing a high dielectric constant over wide temperature range. There is no need to obtain stable temperature dependence to have the core–shell structure.

Fig. 3 is the TEM image of the BCT ceramics without grain growth, showing that the grain boundaries were at most 1 nm

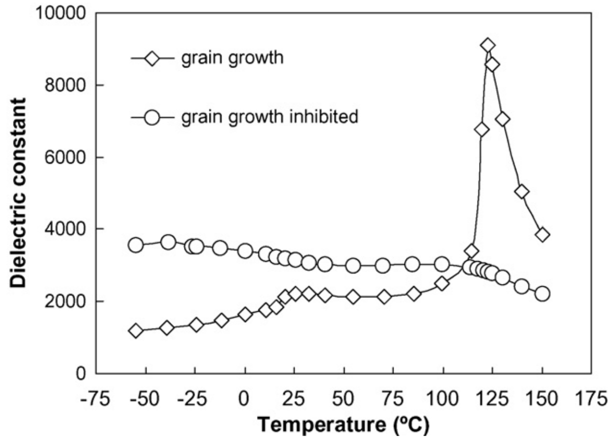

Fig. 2. Temperature dependence of dielectric constant of BCT ceramics. Open circle is a data of BCT ceramics with the grain growth inhibited and open triangle is a data of BCT ceramics with the grain growth during sintering.

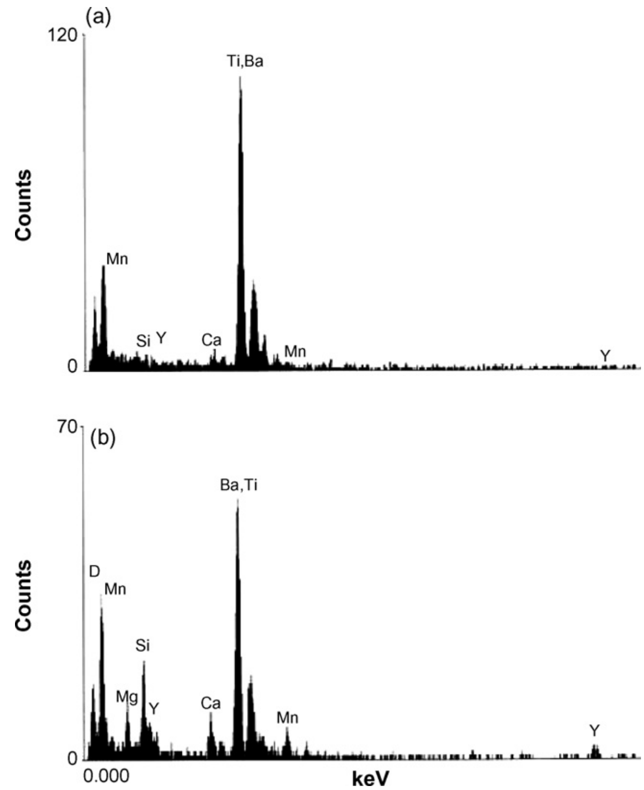

Fig. 4. TEM–EDX charts of grain and grain boundary in BCT ceramics with the grain growth inhibited. (a) Chart obtained for the point 2 nm away from a grain boundary and (b) chart obtained for the point on a grain boundary.

width. Fig. 4 shows the compositional analyses of the BCT ceramics by TEM–EDX, which confirmed that Y, Mg, Mn and Si ions are mostly located at the triple points. These components were undetected inside the grains. Fig. 5 shows the chemical composition analyses data of dilute solution after etching. Si element, which is considered to be dominantly in grain boundaries as shown in Fig. 3, was detected in the solution obtained after 60 min etching. On the other hand, Ba element, which is a main component of BCT grain, was detected in the solution obtained after 120 min etching. This shows that 60 min etching dissolved mainly the grain boundaries of BCT ceramics. Fig. 6 shows (1 1 3) and (3 1 1) diffractions of the calcined powder, the surface of the sintered ceramics, the surface of the 60 min chemically etched ceramics, and of the 300 min chemically etched ceramics. The sintered ceramics show a broad peak characterized as having a large non-uniform distortion in the lattice [11] in comparison with the calcined powder. By etching grain boundaries for 60 min, it is confirmed that the tetragonality of the BCT ceramics recovers to that of the calcined original BCT powder. This means namely, that grain boundaries in the ceramics without grain growth have caused a large stress in the grains, resulting non-uniform distortion. XRD data of the BCT ceramics with grain growth are not shown in this report, but their XRD pattern is similar to that of the calcined powders. The stable temperature dependence in dielectric constant is considered to relate to the existence of grain boundaries yielding a huge stress.

Fig. 7 shows the impedance plane plot of MLCs sample using BCT ceramics. Complex impedance spectroscopy is usually used to analyze the microstructures of ceramics by their conductivity. So far, there are several models proposed for the interpretation of the microstructure [18]. It has been reported in the core–shell dielectrics that the complex impedance planes consist of four responses from the core, the shell, grain boundaries, and the interface between inner electrodes and

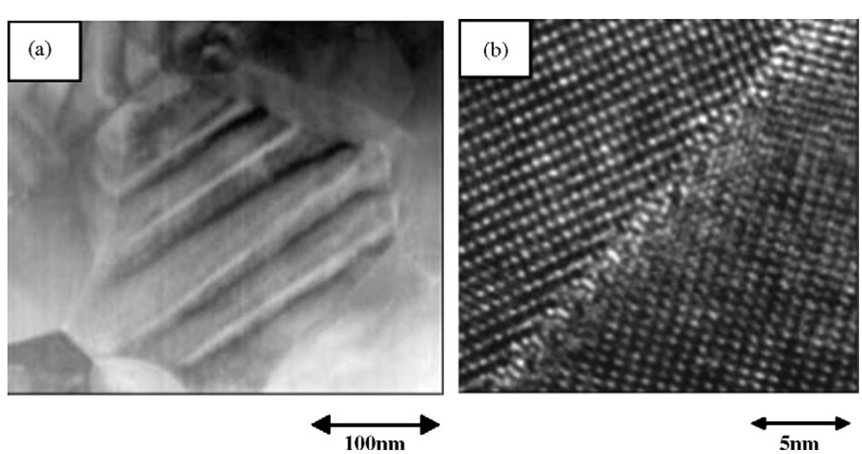

Fig. 3. TEM observations of the BCT ceramics with the grain growth inhibited; (a) TEM image of grains, (b) TEM lattice image of a grain boundary.

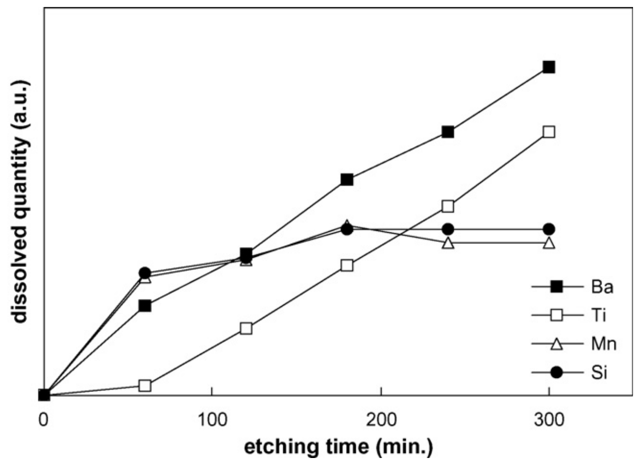

Fig. 5. ICP-AES chemical compositional analyses of dilute solution obtained by etching depending on etching time.

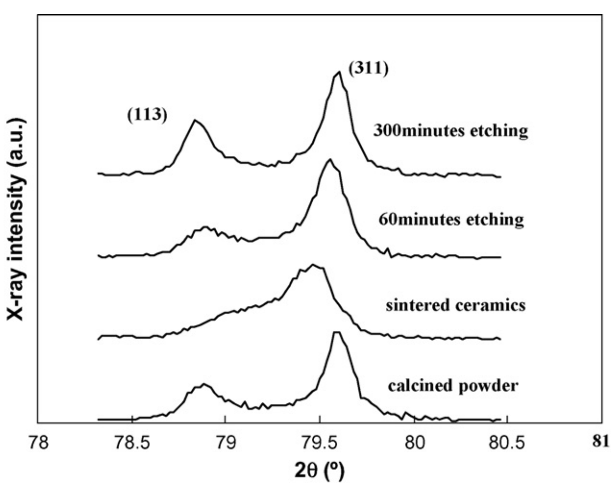

Fig. 6. (1 1 3) and (3 1 1) XRD patterns of the calcined powder, the sintered ceramics and the etched ceramics for 60 and 300 min. BCT ceramics is grain growth inhibited ceramics.

dielectric layers [19]. However, as shown in Fig. 7, BCT ceramics shows an almost single semicircular plot. It is assumed that the single semicircle shows that the BCT ceramics have a more uniform microstructure in comparison with that of the core–shell dielectric ceramics. Fig. 7 also suggests that the resistances of grains and grain boundaries are almost the same. As shown in Fig. 3(b), regarding that the thickness of grain boundary is almost in the range of 1 nm and the thickness of grain is in the range of 100 nm, the resistivity of the grain boundary is assumed to be 2 digits higher than that of the grain. It is considered that the high reliability of BCT ceramics without the core–shell structure depends on the high resistivity of the grain boundary.

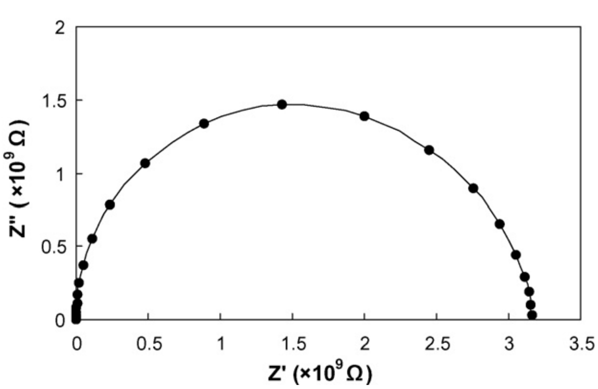

Fig. 7. Impedance spectrum obtained for MLC sample at 200 °C.

4. Summary

Ca-doped BT ceramics without the core–shell structure show a stable temperature dependence of dielectric constant and have high reliability in life tests. In this report, the effect of grain boundaries upon electric properties was investigated. It is confirmed with the chemical analysis of used etching solutions that additional elements were enriched in the grain boundaries, corresponding with TEM–EDX analysis. The tetragonality of BCT ceramics recovered to have high tetragonality, as high as that of the calcined powder, when chemical etching dissolved grain boundaries. It is confirmed that grain boundaries have a strong influence on the stress field within the grains. The complex impedance plane of BCT ceramics without the core–shell structure shows a single semicircle, which suggests that the resistivity of grain boundaries is 2 digits higher than that of grains. It is concluded that the grain boundaries of the BCT ceramics without the core–shell structure have an important roles in BCT dielectric properties.

References

[1] I. Burn, H. Maher, High resistivity $BaTiO_3$ ceramics sintered in CO–CO_2 atmosphere, J. Mater. Soc. 10 (1975) 633–640.
[2] Y. Sakabe, K. Minai, K. Wakino, High dielectric constant ceramics for base metal monolithic capacitors, Jpn. J. Appl. Phys. Suppl. 20 (1981) 147–150.
[3] Y. Sakabe, T. Takagi, K. Wakino, D.M. Smith, Dielectric materials for base-metal multilayer ceramics capacitors, in: J.B. Blum, W.R. Cannon (Eds.), Advances in Ceramics, 19, Am. Ceram. Soc. Inc., Ohio, 1986, pp. 103–115.
[4] Y. Sakabe, Y. Hamaji, T. Nishiyama, New barium titanate based material for MLCs with Ni-electrode, Ferroelectrics 13 (1992) 133–138.
[5] Y. Sakabe, Y. Hamaji, H. Sano, N. Wada, Effects of rare-earth oxides on reliability of X7R dielectrics, Jpn. J. Appl. Phys. 41 (2002) 5668–5673.
[6] H. Kishi, N. Kohzu, J. Sugiro, Y. Iguchi, T. Okuda, Occupational sites and dielectric properties of rare-earth and Mn substituted $BaTiO_3$, J. Eur. Ceram. Soc. 21 (2001) 1643–1647.
[7] S. Sato, Y. Nakano, A. Sato, T. Nomura, Mechanism of improvement of resistance degradation in Y-doped $BaTiO_3$ based MLCCs with Ni electrodes under highly accelerated life testing, J. Eur. Ceram. Soc. 19 (1999) 1061–1065.
[8] X. Liu, S. Cheng, C.A. Randall, The core–shell structure in ultrafine X7R dielectric ceramics, J. Korea Phys. Soc. 32 (1998) S312–S315.
[9] G. Arlt, D. Hennings, G. de With, Dielectric properties of fine-grain barium titanate ceramics, J. Appl. Phys. 58 (4) (1985) 1619–1625.
[10] K. Uchino, E. Sadanaga, T. Hirose, Dependence of the crystal structure on particle size in barium titanate, J. Am. Ceram. Soc. 72 (8) (1989) 1555–1558.
[11] K. Uchino, E. Sadanaga, K. Oohashi, T. Morohashi, H. Yamamura, Particle/grain size dependence of ferroelectricity, in: H.C. Ling, M.F. Yan, AT&T Bell Laboratories (Eds.), Ceramic Transaction, vol. 8, Am. Ceram. Soc. Inc., Ohio, 1989, pp. 107–115.
[12] Y. Sakabe, N. Wada, J. Ikeda, Y. Hamaji, Ceramics for ultra-thin dielectric layer of multilayer ceramic capacitors, in: Proceedings of the 11th IEEE

International Symposium on Application of Ferroelectrics (ISAF), 1998, pp. 565–569.
[13] N. Wada, H. Tanaka, Y. Hamaji, Y. Sakabe, Microstructures and dielectric properties of fine-grained $BaTiO_3$ ceramics, Jpn. J. Appl. Phys. 35 (1996) 5141–5144.
[14] Y. Sakabe, N. Wada, T. Hiramatsu, T. Tonogaki, Dielectric properties of fine-grained $BaTiO_3$ ceramics doped with CaO, Jpn. J. Appl. Phys. 41 (2002) 6922–6925.
[15] N. Wada, Fine-grained ceramics for multilayer ceramic capacitor with ultra-thin dielectric layers, in: The 11th US-Japan Seminar on Dielectric & Piezoelectric Ceramics, Extended Abstract, 2003, 15–22.
[16] N. Wada, Dielectric nano-powders applied to multilayer ceramic capacitors with ultra-thin dielectric layers, J. Soc. Powder Technol. Jpn. 41 (2004) 35–43.
[17] I. Nitta, X-sen Kesshougaku Ge in Japanese (X-ray Crystallography), vol. 2, Maruzen, Tokyo, 1961, p. 618.
[18] N. Hirose, A.R. West, Impedance spectroscopy of undoped $BaTiO_3$ ceramics, J. Am. Ceram. Soc. 79 (1996) 1633–1641.
[19] H. Chazono, H. Kishi, DC-electrical degradation of the BT-based material for multilayer ceramic capacitor with Ni internal electrode: impedance analysis and microstructure, Jpn. J. Appl. Phys. 40 (2001) 5624–5629.