

# Investigation of grain boundaries influence on dielectric properties in fine-grained BaTiO<sub>3</sub> ceramics without the core–shell structure

Nobuyuki Wada<sup>\*</sup>, Takashi Hiramatsu, Toshiyuki Tamura, Yukio Sakabe

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

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## Abstract

Grain boundaries of the Ca-doped and fine-grained BaTiO<sub>3</sub> (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.

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## 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

<sup>\*</sup> Corresponding author.

*E-mail address:* [nobuwada@murata.co.jp](mailto:nobuwada@murata.co.jp) (N. Wada).

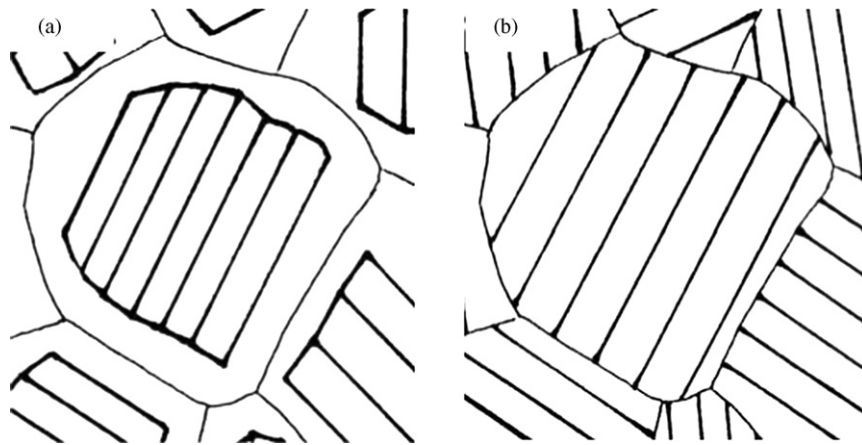


Fig. 1. Schematic diagrams of the core-shell structure (a) and the non-core-shell structure (b). Solid lines in grains mean the ferroelectric domain structure.

these newly developed fine-grained ceramics had already been applied to MLCs with 1  $\mu\text{m}$  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  $\text{Ba}(\text{OH})_2$ , Ti alkoxide, and  $\text{CaCl}_2$ . Raw materials were mixed above 80  $^\circ\text{C}$  for 3 h in the solution to pH 12. After washing, drying and calcining at 1050  $^\circ\text{C}$  in air, they were then mixed with 1 mol%  $\text{MgCO}_3$ , 0.2 mol%  $\text{MnCO}_3$ , 2 mol%  $\text{SiO}_2$ , and 0.5 mol%  $\text{Y}_2\text{O}_3$ . 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  $\mu\text{m}$ . 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 ( $1.6 \times 10^{-11}$  MPa  $\text{O}_2$  at 1150  $^\circ\text{C}$  or  $7.2 \times 10^{-10}$  MPa  $\text{O}_2$  at 1300  $^\circ\text{C}$ ) 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  $\text{V}_{\text{rms}}/\mu\text{m}$ , 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  $\text{V}/\mu\text{m}$  at 200  $^\circ\text{C}$ , 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

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