Formation of Core-Shell Structure in BaTiO$_3$ Grains

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ABSTRACT

To understand the formation of core-shell structure in BaTiO$_3$ (BT) grains in multilayer ceramic capacitors, specimens were prepared with BT powders mixed with Y and Mg, and their microstructures were investigated with scanning electron microscopy, x-ray diffractometry, and transmission electron microscopy. Microstructural investigation showed that Y dissolved easily in BT lattice to a certain depth inside of the grain, whereas Mg tended to stay at grain boundaries rather than become incorporated into BT. It was considered that in case of Y and Mg addition in a proper ratio, Y could play a dominant role in the formation of shell leading to a slight dissolution of Mg in the shell. Next, the effects of ball-milling conditions on the core-shell formation were studied. As the ball-milling time increased, the milled powders did not show a significant change in size distribution but rather an increase of residual strain, which was attributed to the milling damage. The increase in milling damage facilitated the shell formation, leading to the increased shell portion in the core-shell grain.

Key words: BaTiO$_3$, Core-shell, Additive, Milling

1. Introduction

Development of Multilayer Ceramic Capacitors (MLCC's) of a higher capacitance and a smaller chip size requires a structure in which hundreds of dielectric layers less than 1 μm thick are alternately stacked with inner electrodes. In such a thin layered structure, controlling the microstructure is difficult due to the effect of adjacent layers; the increased electric field intensity applied to the dielectric layer makes the reliability issue of great significance. For 1 μm thick layers, to meet the requirements for the temperature dependence of the capacitance and the reliable performance in MLCC, BaTiO$_3$ (BT) grains need to be about 200 nm or less in size, and form a so-called ‘core-shell’ structure, in which the additive elements are partially dissolved in BT grains. The core-shell grain consists of the core region, pure BT with a ferroelectric tetragonal structure, surrounded by the shell, which contains some additive elements and is pseudocubic.1-4)

The most important thing in forming a core-shell structure is the combination of the proper additives, which leads to the reaction with dielectric grains. In the BT-MgO-Ho$_2$O$_3$ system, Kishi et al. suggested a mechanism whereby Mg reacts with BT to form a shell at low temperatures and at a higher temperature, Ho reacts with the shell but its diffusion into the core is inhibited by Mg.5) Chazono et al. reported that Nb and Co substituted for Ti-site in BT to form a shell in the BT-Nb$_2$O$_5$-Co$_3$O$_4$ system.6,7) As for the composition of the shell, several different elements such as Zr, Yb, Sr, and Y have been reported.8,9) In spite of the literature, it is not clearly understood what the predominant element is to form a shell and how the shell is formed.

In addition to the material aspect, process conditions for MLCC fabrication also play a role in the core-shell formation. Although the sintering parameters such as soak temperature and atmosphere are of significance for the microstructure of MLCC, the physical, chemical, or mechanical properties of the starting powders could also have an influence on microstructure. Mizuno et al. reported the effects of ball milling conditions on the chip microstructure.10,11) In their study, the dielectric grains were categorized into three groups - core, shell, and core-shell grains - and then, their number dependence on milling conditions was examined. This observation, however, is not sufficient to clearly understand how the milling condition could affect the shell formation.

In the present study, BT ceramics added with Y and Mg were prepared and their microstructures were investigated to understand the role of each additive element in the formation of the core-shell structure. In addition, after ball milling of different durations, the powder characteristics and their effects on the microstructure of sintered specimen were studied, aiming at understanding the relationship between chip microstructure and process conditions.
2. Experimental Procedure

2.1. Specimen preparation

It is known that at grain sizes below about 0.7 µm, the ferroelectricity of BT strongly decreases and its structure changes from tetragonal to pseudocubic. In the case of MLCC consisting of 200 nm dielectric grains, it is difficult to distinguish ferroelectric core from nonferroelectric shell in the grain. As a result, to facilitate the formation of the core-shell structure and its observation in the BT grain, specimens using BT powders of 400 nm nominal size with additives in the MgO-Y₂O₃-BaSiO₃ system were prepared.

The starting powders were hydrothermally synthesized BaTiO₃ (Sakai), MgCO₃ (Kyorix), Y₂O₃ (Rhodia), BaCO₃ (Sakai) and SiO₂ (Kojundo Chemical). Aimed at understanding the contribution of additive elements to shell formation, we set the composition of specimens as shown in Table 1. The powders were weighed according to the nominal compositions, and mixed in water with dispersant by ball-milling for 12 h. The mixed powders were dried at 120°C, granulated with polyvinyl alcohol, and pressed uniaxially into disks of 15 mm diameter. The disks were baked at 400°C for binder removal and annealed at 700°C for 1 h in order to make them mechanically robust during the following processes. The specimens were sintered at 1350°C for 2 h in N₂-H₂-O₂ atmosphere.

2.2. Microstructural analysis

Bulk density of sintered specimen was measured using Archimedes method. The disks were polished down to 0.3 µm grade, chemically etched, and then observed by scanning electron microscope (SEM, LEICA S440) to examine the grain size distribution.

The core-shell structure of BT grains was investigated in terms of x-ray diffractometry (XRD), differential scanning calorimetry (DSC), and transmission electron microscopy (TEM). To check tetragonality (c/a) of the dielectric grains, XRD measurements (Rigaku, RINT 2200HF, Cu Kα) were carried out on powder or bulk specimens mainly in the range of 2θ values of 44 to 46.5°, covering (002) and (200) peaks of tetragonal BT, at 0.02° step. DSC (Perkin Elmer DSC7) measurements were performed up to 150°C in N₂ atmosphere to check the tetragonal to cubic transition peak at about 125°C; the integrated intensity of the peak corresponds to the proportion of the tetragonal core region.

TEM samples were prepared using tripod polishing followed by ion beam thinning (Gatan PIPS), and investigated using a Tecnai G2 F20 microscope (FEI) operating at 200 kV.

3. Results and Discussion

3.1. Contribution of Y and Mg to the formation of core-shell structure

Fig. 1 shows the change of bulk density according to the additive composition. The density of the specimen with proper amounts of Y and Mg was found to be from 5.87 to

![Fig. 1. Bulk density of the disk sintered at 1350°C as a function of Mg amount.](image)

Table 1. Composition of Ceramic Specimens

<table>
<thead>
<tr>
<th>Notation</th>
<th>BaTiO₃</th>
<th>MgCO₃</th>
<th>Y₂O₃</th>
<th>BaCO₃</th>
<th>SiO₂</th>
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</tr>
<tr>
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<td>2.0</td>
<td>2</td>
<td>2.5</td>
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</tr>
<tr>
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<td>1.5</td>
<td>2.5</td>
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</tr>
<tr>
<td>2Y4Mg</td>
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<td>1.0</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>0Y6Mg</td>
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<td>6.0</td>
<td>0</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>R</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>2.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

[Unit: mol]

![Fig. 2. Scanning electron micrographs of the cross sections of disks sintered at 1350°C: (a) 6Y0Mg, (b) 4Y2Mg, (c) 3Y3Mg, (d) 2Y4Mg, (e) 0Y6Mg, (f) R specimen.](image)
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5.91 g/cm$^3$, comparable to that of the specimen without additives (5.85 g/cm$^3$). An increase of the amount of Mg induced a gradual decrease of the density while the specimen with only Y had the lowest density (5.26 g/cm$^3$), indicating that excessive addition of Y reduced the sinterability of BT grains.

The cross sectional SEM images of the sintered disks are shown in Fig. 2. Specimen 'R' consists of grains about 10 times larger than those of the specimens with additives; the average grain size was 4.74 (R), 0.365 (6Y0Mg), 0.352 (4Y2Mg), 0.355 (6Y3Mg), 0.349 (2Y4Mg), and 0.337 µm (0Y6Mg). The sintered specimens with additives showed similar grain sizes slightly less than the nominal raw powder size and almost no grain growth. The '6Y0Mg' specimen had a relatively porous microstructure, which was attributed either to the low bulk density or to a selective etch-out of secondary phases during the chemical etching process.

Fig. 3 shows the XRD patterns of the powders dried after ball-milling and the disks sintered at 1350°C. The powders showed similar XRD patterns, irrespective of the additive composition; the slight increase of intensity between (002) and (200) peaks is considered to result from particle size reduction during ball-milling (Fig. 3(a)). The sintered disks, however, showed different behavior according to the additive composition. While in specimen 'R' the peaks reflected increased crystallinity (the appearance of $K_{\alpha}$ peak), tetragonality, and K-factor (ratio of the intensity of (200) peak to that between (002) and (200) peaks), which mainly resulted from the grain growth of BT, the specimens with additives showed one peak corresponding to a pseudocubic structure, from which it is known that the reaction of additives with BT enhances the intensity between (002) and (200) peaks.$^{31}$ This result implies the possibility of a reaction between additives and BT to some extent, which could be investigated using TEM.

In specimen '6Y0Mg', TEM observation confirmed the porous microstructure again, and showed two interesting features: there were some features like strain contrast in the grain and most grains did not show 90° domains as shown in Fig. 4(a). In some cases, there were shell-like parts observed inside of the grain; an energy dispersive spectrometry (EDS) line profiling across that region revealed that the Y concentration was preserved to a certain depth from the grain boundary and decreased toward the inside of the grain (Fig. 4(b)). Y has been reported to substitute for the Ba-site at low doping concentrations, and as its concentration increases, it begins to dissolve in Ti-site, up to 12 at% at 1515°C.$^{14}$ Consequently, in the case of the addition of 6 mol Y, it is considered that Y was easily dissolved in the dielectric grain, leading to the reduced tetragonality and disappearance of domains. The specimens added with proper ratios of Y to Mg (Y:Mg=4:2, 3:3, 2:4) showed well-developed and easily-observed core-shell grains; a typical core-shell grain observed in '2Y4Mg' specimen is shown in Fig. 5(a). The core region is clearly distinguished from the shell in terms of the existence of domain boundaries. EDS line profile in Fig. 5(b) indicated that the concentration of Y decreased abruptly across the shell-to-core boundary and a small amount of Mg and Zr was also contained in the shell. Although the shell composition was slightly varied from grain to grain, it was generally confirmed that Y was a dominant additive element in forming the shell and Mg made a

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**Fig. 3.** XRD patterns of the specimens with various additive compositions; (a) powders dried after ball-milling, (b) disks sintered at 1350°C.
Fig. 4. (a) Transmission electron micrograph of typical dielectric grains in ‘6Y0Mg’ specimen; No ferroelectric domains are visible. (b) and (c) EDS line profile on a grain showing the concentration gradient of Y within the grain.

Fig. 5. (a) Transmission electron micrograph of a typical core-shell grain in ‘2Y4Mg’ specimen, (b) EDS line profile on the grain in (a) indicating that Y is a dominant element in forming a shell.
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contribution to some extent. The Zr detected with Mg was attributed to contamination from ZrO$_2$ balls during the ball milling process.

In specimen '0Y6Mg', which contained Mg only, the domain boundary was well observed, but the shell-like region was hardly detected, as shown in Fig. 6(a). Moreover, EDS line profile did not show any concentration variation of Mg and Zr over the whole grain (Fig. 6(b), (c)). Wada et al. reported that for BT powders synthesized hydrothermally and calcined at 800$^\circ$C, the maximum concentration of Mg dissolved in BT was about 0.15 wt%.$^{15}$ Therefore, the EDS result in Fig. 6(c) implies two possibilities: no dissolution of Mg in BT grain or the dissolution of a very small amount of Mg that was below the detection limit of our TEM EDS equipment. The XRD pattern of specimen '0Y6Mg' in Fig. 3(b), however, showed a pseudocubic peak as in other specimens of different additive compositions, which indicates that the additive would react with the dielectrics. To judge whether a shell has been formed, specimen '0Y6Mg' needs to be examined in a more detailed manner. In addition to the difficulty of observing a shell, the TEM investigation of specimen '0Y6Mg' revealed another interesting fact: the existence of a liquid phase at the grain boundary. Scanning transmission electron microscopy dark-field (STEM DF) image showed a dark contrast layer at the boundary between two adjacent dielectric grains, and EDS analysis detected relatively high intensities of Si and Mg at the same region. From these results, it is considered that Mg does not dissolve easily in the dielectric grain, compared to Y, but rather tends to stay in the liquid phase or even form a secondary phase. In the specimen with Mg and Y, as shown in Fig. 5, the concentration of Mg in the shell region was found to be slightly higher than that in case of the addition of Mg only (Fig. 6), which implies that the lattice deformation resulting from the incorporation of Y into BT could make Mg dissolve more readily. As a result of the TEM analyses, it is considered that Y readily dissolves in the BT lattice whereas Mg tends to stay at the grain boundary instead of incorporating into BT. It is also considered that to form a core-shell structure, both Y and Mg are required in an appropriate ratio so that Y can play a domi-

Fig. 6. (a) Transmission electron micrograph of a typical dielectric grain showing apparent domains in '0Y6Mg' specimen, (b) and (c) EDS line profile showing no concentration variation of Mg and Zr across one grain.

![Transmission electron micrograph of a typical dielectric grain showing apparent domains in '0Y6Mg' specimen](image1)

![EDS line profile showing no concentration variation of Mg and Zr across one grain](image2)
3.2. Effects of milling damage on the formation of core-shell structure

For ‘2Y4Mg’, whose composition turned out to have a well-developed core-shell structure, ball-milling time among the various process parameters was varied at 12, 24 and 48 h to investigate its effects on specimen microstructure. Since the powders of BT and additives in different sizes were mixed as starting materials, it was somewhat difficult to verify the change of powder size distribution through ball-milling from the SEM images of ball-milled powders. However, the sizes of more than 150 primary particles in SEM images were measured to give results showing that D$_{50}$=0.354, 0.294, and 0.294 µm for 12 h, 24 h, and 48 h milling, respectively.

Specific surface area measurement (BET) of the milled powders revealed that the BET value of the powder increased in a linear proportion to the milling time; 4.583 for 12 h, 5.931 for 24 h, and 9.191 m$^2$/g for 48 h milled powder. This increase of powder BET was not attributed to the size reduction of powder, as shown in the SEM images, but rather to an increase of surface roughness due to the accumulated milling damage.

If the powder was subject to milling damage without any significant size reduction, then the residual strain of powder could be estimated using XRD or Raman spectroscopy. Fig. 7 shows XRD patterns of (002)/(200) and (113)/(311) peaks of the powders after ball-milling. As the milling time increased, K-factor of the peaks gradually decreased. In addition, tetragonality of the powders determined using (002)/(200) peak positions also decreased; 1.0092 for 12 h, 1.0080 for 24 h, and 1.0080 for 48 h milling. This indicates that excessive milling deteriorates the crystallinity of powders. Two factors affecting the broadening of XRD peaks are residual strain and size of the diffracting particles in the specimen; those effects can be expressed using the following Williamson-Hall eq.:

$$B \cos \theta = 2 \eta \sin \theta - \frac{k}{D}$$

where $B$ is full-width-at-half-maximum (FWHM) of each XRD peak, $\theta$ Bragg angle, $\eta$ residual strain, $D$ particle size, $\lambda$ wavelength of x-ray, and $k$ equation constant. Plotting $B \cos \theta$ vs. $2 \sin \theta$ with the values of Bragg angle and FWHM of each peak in the XRD pattern gives a value for strain from the slope and that for particle size from the intercept to Y-axis. The Williamson-Hall plots determined from (001)/

Fig. 7. XRD patterns of the powders after ball-milling for a different time; (a) (002)/(200), (b) (113)/(311) peaks.

Fig. 8. $B \cos \theta$ vs. $2 \sin \theta$ plots determined from (001), (100), (002), (200), (300) peaks of the powders milled for different times.
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The (100), (002)/(200), and (300) peaks of each ball-milled powder are shown in Fig. 8; (003) peak was not included in the plot due to the difficulty in measuring FWHM. As the milling time increased, the W-H plot became steeper, making the strain value linearly proportional to the milling time; 0.141 for 12 h, 0.183 for 24 h, and 0.251 for 48 h. From the results of SEM, BET, and XRD of the powders, it is considered that the increase of ball-milling time from 12 h to 48 h did not induce any considerable change in the powder size distribution but resulted in increased milling damage in the powders, which would influence the microstructure of the sintered specimen.

The bulk density of the disks, which were formed with the previously described powders and sintered at 1350°C, was almost unchanged; 5.87 for 12 h, 5.82 for 24 h and 5.82 g/cm$^3$ for 48 h milling. The grain size distribution measured from the SEM images did not show any noticeable increase from the values of milled powders measured from SEM images; $D_{50}=0.349$ for 12h, 0.351 for 24h, and 0.301 µm for 48h milling. The (002)/(200) XRD patterns of the sintered disks showed pseudocubic peaks of a similar shape regardless of the milling time; the peaks are similar to the ones shown in Fig. 3(b). As mentioned previously, the formation of core-shell structure in the dielectric grains would change the XRD peaks of bulk specimen from tetragonal to pseudocubic. However, it is difficult quantitatively to deduce the variation of fraction between core (tetragonal) and shell (pseudocubic) from the change of XRD peak shape.

The TEM investigation of the microstructure of each specimen showed a general tendency that the core-shell grain in the specimen with a longer milling time had a thicker shell. For some cases, however, a thick shell was observed in a large grain. Consequently, it is more reasonable in the estimation of shell fraction to compare the shell width to grain size ratio rather than to measure the shell thickness only.

In the study of the effects of milling damage on the ceramic microstructure, Mizuno et al. observed about a hundred grains by TEM, classified them into core grain, shell grain and core-shell grain, then correlated the variation of the number of each grain to the process conditions.

However, compared to their approach, the variation of shell portion in one core-shell grain in the present study seems to be able to more reasonably reflect the shell formation influenced by the milling damage. As a result, the grain size and shell width were measured for all core-shell grains observed in the TEM images of each specimen, and the ratios of shell width to grain size were plotted in Fig. 9. Fig. 9 revealed that the shell portion in the dielectric grain tended to increase with the increasing milling damage. This result could be understood based on the fact that the increased milling time induces an increase in the residual strain and surface roughness of the powders, resulting in the enhanced surface activity of powders, which in turn facilitates the reaction between the dielectric and additives during sintering to promote the shell formation. Although every core-shell grain showed slightly different concentration for shell composition, the shells observed in the specimen with a longer milling time generally had an increased amount of Zr. This was attributed to the increased amount of Zr contamination during the prolonged milling process.

The increase in the shell portion observed in TEM investigation was confirmed by DCS analysis, as shown in Fig. 10. The area under the peak at about 125°C corresponding to the latent heat of phase transition per unit mass decreased with the increasing milling time, which is consistent with
the TEM results showing the increased shell portion, i.e., the decreased core portion in the grains.

4. Conclusions

To understand the formation of core-shell structure in \( \text{BaTiO}_3 \) grains, 400 nm BT powders were mixed with Y and Mg in various ratios to form ceramic disks and the microstructure of the sintered disks was investigated. Compared to BT without additives, specimens with the addition of additives were found to have inhibited growth of the dielectric grains, particularly showing a much reduced sinterability in the case of Y addition. For the specimen with only Y added, Y dissolved easily in the BT lattice, making the domains in the core region disappear, whereas Mg tended to stay in the liquid phase instead of incorporating into BT. It is considered that in the case of addition of Y and Mg in a proper ratio, Y could play a dominant role in the formation of a shell when the excessive dissolution of Y in BT was suppressed by Mg.

To study the effects of process conditions on the core-shell formation, the powders were ball-milled for different times. As the milling time increased, the milled powders did not show a significant difference in size distribution; there was an increase in BET and residual strain confirmed through XRD and Raman spectroscopy, which was attributed to the milling damage. The change of powder characteristics did not induce any difference in the sinterability but influenced the formation of core-shell structure. The increase in milling damage facilitated the shell formation, leading to the increased shell portion in the core-shell grain.

REFERENCES