Formation of grain boundary second phase in BaTiO$_3$ polycrystal under a high DC electric field at elevated temperatures

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The microstructure of the damaged area created during a flash sintering event in BaTiO$_3$ was examined by high resolution transmission electron microscopy (HRTEM) and electron energy loss spectrometry (EELS) measurement. A DC electric field of 133 V/cm was applied to a fully-densified BaTiO$_3$ body prepared by conventional sintering, and the specimen temperature was elevated at a constant heating rate. The flash sintering event, at which the electric current in the specimen abruptly increases at the threshold field and temperature, took place at 890°C. After the flash event, tunnellike physical damage was observed in the direction of the field through the specimen. Formation of grain boundary second phase layers around the damaged area was confirmed by HRTEM observations. The grain boundary second layer was a crystalline phase with a low Ba/Ti atomic ratio of less than one. The temperature in some of the grain boundaries must increase by Joule heating during the flash event, thus the chemical composition in the vicinity of the grain boundaries changed due to vaporization of the Ba cations, resulting in the formation of the grain boundary second phase layers.

Key-words : BaTiO$_3$, Flash sintering, Grain boundary, TEM

1. Introduction

Electric current/field assisted sintering techniques have demonstrated accelerated sintering densification of ceramic materials compared to conventional sintering. In particular, flash sintering, at which sintering densification occurs almost immediately at a threshold condition of temperature and applied electric field, has shown to reduce the sintering temperature and sintering time. For instance, 3 mol % Y$_2$O$_3$-stabilized tetragonal ZrO$_2$ (TZP) green compacts can be fully densified at 850°C in 5 s under an applied field of 120 V/cm without any pressure, while the conventional sintering temperature and time required for full densification of the TZP are about 1400°C and a few hours, respectively. Flash sintering has been applied to various ceramic materials such as Co$_3$MnO$_5$, Mg-doped Al$_2$O$_3$, SrTiO$_3$, SiC, ZnO, SnO$_2$, Y$_2$O$_3$, TiO$_2$, CeO$_2$, and BaTiO$_3$.

In our previous study, the consolidation behavior of undoped BaTiO$_3$ in terms of the electric field assisted sintering has been investigated in detail. BaTiO$_3$ can be densified at 1020°C under the applied field of 100 V/cm with the current limit of 5 mA/mm$^2$, while conventional, pressureless sintering requires 1300°C for 5 h. Flash sintering also occurs in BaTiO$_3$ under the field of more than 100 V/cm, however, full densification cannot be achieved by the flash; tunnellike physical damage was created in the direction of the electric field through the specimen. The same results have also been reported by M’Peiko et al. The formation of the physical damage must be related to the electrical discharge of BaTiO$_3$ during the flash sintering. The detailed microstructures of the damaged areas in BaTiO$_3$, however, have not yet been investigated. In the present study, the microstructure in the vicinity of the damaged area was observed by transmission electron microscopy (TEM). A grain boundary second phase layer, which suggests localized heating at the grain boundaries, has been found as will be described in the following sections.

2. Experimental procedure

Commercially available BaTiO$_3$ powder (purity >99.9%, Lot. No. 1308607: Sakai Chemical Industry, Japan) was used as the starting material. According to the manufacturer’s report, the average initial particle size and Ba/Ti atomic ratio of the powder is 0.1 µm and 1.000, respectively. The raw powders were uniaxially pressed at 30 MPa into a rectangular bar, then cold-isostatically pressed at 100 MPa. The compacted powder was provided with two small holes. The green compact was sintered in air at 1300°C for 5 h in order to obtain a densified body with a relative density of about 98%. An average grain size determined by π/2 times an average linear intercept length of 300 grains from optical microscopy images was 24.5 µm. The dimensions of the sintered body were 1.6 mm in thickness, 7.8 mm in width, and 24.7 mm in length. The interval between the two small holes was 15.0 mm. The sintered specimen was suspended inside an electric furnace by Pt wires through the two small holes by employing Pt-based paste. Furnace temperature was raised at the heating rate of 300°C/h under a DC electric field of 133 V/cm. The electric field was applied through the Pt wires by a stabilized power supply (HEP-3 2100: Matusada Precision, Japan) at a current limit of 500 mA. During the heating under the electric field, the specimen current was monitored. When the specimen current reached the limited value, the furnace and power supply were kept for 1 min, then switched off.

As shown in the results, tunnellike damage was produced in the specimen heated under the electric field. The microstructure...
of the specimen after heating under the field was observed by an optical microscope and a high resolution transmission electron microscope (HRTEM, ARM-200F, JEOL Ltd.). Thin foils for the TEM observations were prepared by a conventional procedure including Ar ion-beam milling. In order to protect the fragile portion of the specimen such as the damaged area, the specimen was impregnated with epoxy, mechanically ground, polished and then ion-beam milled. As shown below, grain boundary second phases were observed in the specimen after the heating experiment under the applied field. The chemical compositions of the localized portion in the specimen were determined by electron energy loss spectrometry (EELS; Enfina spectrometer, Gatan, USA) measurements in the HRTEM. The EELS measurement was carried out on five different BaTiO$_3$ grains and grain boundary phases by using a probe size of 50 nm. The atomic structure of the second phases was observed by high-resolution high-angle annular dark field (HAADF)-scanning transmission electron microscopy (STEM) method.

3. Results

A plot of the specimen current under the field of 133 V/cm as a function of the furnace temperature is shown in Fig. 1(a). The specimen current gradually increased with the increasing furnace temperature, then abruptly increased at the temperature of 890°C. The gradual increase in the specimen current before the surge of the current is attributed to the decrease in the resistivity due to the higher temperature. Appearance of the current surge has been observed during the flash sintering process of BaTiO$_3$.\textsuperscript{13,14} The flash event, where the electric resistivity drastically decreases under the threshold field strength and temperature, took place even in the densified BaTiO$_3$ polycrystal. Figures 1(b) and 1(c) show optical micrographs after the flash event. After the flash experiment, tunnellike physical damage with a diameter of about 0.5 mm was produced between the Pt electrodes through the specimen, as shown in Fig. 1(b). The color around the hole was bluish black, indicating reduction of the specimen during the flash event. In addition, there can be seen many small holes with diameters of about a few dozen micrometers around the damage, as shown in Fig. 1(c). Their shapes are almost round. The appearance of the small holes suggests that some component in the damaged area evaporated due to local heating.

A typical bright field TEM image in the vicinity of the damaged area is shown in Fig. 2(a). Linear second phases were found around the physical damage as indicated by arrow A in Fig. 2(a). In Fig. 2(a), two BaTiO$_3$ grains adjacent to the second phase have different crystalline orientations, as shown in the selected electron diffraction (SAD) patterns inserted in the corresponding grains. The second phase layer is therefore an intergranular phase (produced at the BaTiO$_3$ grain boundary), not an intragranular phase. The inset SAD at the right top of Fig. 2(a) is taken from the second phase. The SAD revealed that the

![Fig. 1.](image1.png)  
![Fig. 2.](image2.png)

Fig. 1. (a) Electrical current profile for the heating experiment under the applied field of 133 V/cm as a function of the furnace temperature. (b) Optical micrograph of cross-sectional surface of the specimen after the flash event. (c) Enlarged optical micrograph around the tunnellike damage.

Fig. 2. (a) A typical bright field TEM image in the vicinity of the damaged area. Second phase layer is found at a grain boundary as indicated by arrow A. (b) HAADF-STEM image of a second phase layer. (c) A typical HRTEM image of the second phase.
second phase is in direct contact to the BaTiO_3 grains as indicated by employing EELS with the probe size of 50 nm. This suggests the occurrence of rapid solidification. In addition, the second phase is in direct contact to the BaTiO_3 grains as indicated by the arrow in Fig. 2(c). The Ba/Ti atomic ratio cannot be determined by energy dispersive X-ray spectroscopy (EDS), because the X-ray lines of Ba and Ti overlap with each other. In this study, the Ba/Ti atomic ratio of the second phase was determined by employing EELS for five different BaTiO_3 grains and second phases are summarized in Table 1. The raw data of the Ba/Ti atomic ratio in the second phase are in reasonable agreement with each other, nevertheless the absolute values deviate from unity for the stoichiometric BaTiO_3. The ratios of the second phases are also in good agreement with each other, and significantly lower than those of the BaTiO_3 grains. The average value of the experimental ratios in the BaTiO_3 grains is converted to 1 by using the proportionality coefficient of 1.47 as a first approximation. The Ba/Ti atomic ratio of the second phase was estimated to be 0.34 by using the same proportionality factor. The low Ba/Ti atomic ratio in the second phase probably results from vaporization of the Ba cations. In direct vapor deposition technique for the production of BaTiO_3 thin films, a difference in the vapor pressure between Ba and Ti in BaTiO_3 has been pointed out; electron beam evaporation experiments of BaTiO_3 indicated that the vapor pressure of Ba is significantly higher than that of Ti. The present result shows the same tendency as the literature, though the vaporization procedures are different.

Figure 3 shows an example of HRTEM image taken from a grain boundary without any second phase layer in the damaged area. SAD patterns for the respective grains are shown as insets. SAD patterns show that the incident beam direction is nearly parallel to the [011] directions of the BaTiO_3 grains with the rotation angle of about 70°. The orientation relationship of the two grains is near-asymmetric 2Σ with the grain boundary planes of (411) and (011). The observed grain boundaries without second phase layers were often coherent boundaries, as shown in Fig. 3. It would seem that the second phase layers tend to be created at random grain boundaries, not at coherent grain boundaries. A conventional TEM bright field image and HAADF-STEM image of a second layer is shown in Figs. 4(a) and 4(b), respectively. The second phase consists of fine rod-like crystals. The fine structure suggests the occurrence of rapid solidification. In addition, the second phase is in direct contact to the BaTiO_3 grains as indicated by the arrow in Fig. 2(c). The Ba/Ti atomic ratio cannot be determined by energy dispersive X-ray spectroscopy (EDS), because the X-ray lines of Ba and Ti overlap with each other. In this study, the Ba/Ti atomic ratio of the second phase was determined by employing EELS for five different BaTiO_3 grains and second phases are summarized in Table 1. The raw data of the Ba/Ti atomic ratio in the second phase are in reasonable agreement with each other, nevertheless the absolute values deviate from unity for the stoichiometric BaTiO_3. The ratios of the second phases are also in good agreement with each other, and significantly lower than those of the BaTiO_3 grains. The average value of the experimental ratios in the BaTiO_3 grains is converted to 1 by using the proportionality coefficient of 1.47 as a first approximation. The Ba/Ti atomic ratio of the second phase was estimated to be 0.34 by using the same proportionality factor. The low Ba/Ti atomic ratio in the second phase probably results from vaporization of the Ba cations. In direct vapor deposition technique for the production of BaTiO_3 thin films, a difference in the vapor pressure between Ba and Ti in BaTiO_3 has been pointed out; electron beam evaporation experiments of BaTiO_3 indicated that the vapor pressure of Ba is significantly higher than that of Ti. The present result shows the same tendency as the literature, though the vaporization procedures are different.

Figure 3 shows an example of HRTEM image taken from a grain boundary without any second phase layer in the damaged area. SAD patterns for the respective grains are shown as insets. The grain boundary is free from the second phase layer even in the damaged area. SAD patterns for the respective grains are shown as insets.

![HRTEM image of the second phase](image)

**Figure 3.** An HRTEM image taken from a grain boundary in the damaged area without a second phase layer.

**Table 1.** Ba/Ti atomic ratio determined by EELS measurement for five different BaTiO_3 grains and grain boundary second phase layers. The average values of the experimental Ba/Ti ratios are converted by using the proportionality coefficient of 1.47 (see text)

| Ba/Ti raw data/at% | Average Ba/Ti atomic ratio | Converted Ba/Ti atomic ratio |
|-------------------|---------------------------|-----------------------------|
| BaTiO_3 grains    |                           |                             |
| #1    | #2    | #3    | #4    | #5    | 0.68 | 1    |
| 38/62 | 41/59 | 42/58 | 41/59 | 41/59 | 0.68 | 1    |
| Secondary phases |                           |                             |
| 19/81 | 19/81 | 19/81 | 19/81 | 19/81 | 0.23 | 0.34 |

As shown in Table 1, all of the observed second phases have the same Ba/Ti atomic ratios of 0.34. This fact suggests that an unknown phase with a low Ba composition exists in the BaO–TiO_2 system. The precise crystal structure could not be determined in this study, because the width of the second phase is too small to be analyzed in detail. Based on the Ba/Ti atomic ratio, the possible compositions of the second phase in the BaO–TiO_2 system are such as Ba_6Ti_17O_40 (Ba/Ti = 0.353) and Ba_4Ti_13O_30 (Ba/Ti = 0.308). For instance, Ba_6Ti_17O_40 is stable below 1350°C, and exists with BaTiO_3 below 1332°C. The temperature at some grain boundaries in the BaTiO_3 probably increased by Joule heating during the flash event, and the chemical composition at the grain boundaries must change due to the vaporization of the Ba cations, resulting in the formation of the second phase layers along the grain boundaries.

The flash event is characterized by the abrupt rise in the specimen current occurring at a threshold field and temperature. The occurrence of the flash event is often discussed in terms of induced charge carriers due to the DC electric field in addition to the Joule heating effect. For instance, the first study of the flash sintering of TZP revealed that the specimen temperature should be much higher than that produced by the Joule heating, and suggested that extrinsic Frenkel pairs, i.e., the combination of...
where $T_0$ is the furnace temperature, $a$ is the total surface area of the specimen (assumed to be the gauge section) equal to $2.82 \times 10^{-4} \text{m}^2$, and $\sigma$ is the black body radiation constant equal to $5.67 \times 10^{-8} \text{W/m}^2\text{K}^4$. At the onset of the flash, the input power $W$ was 101 W. The specimen temperature calculated from Eq. (1) was 1891°C at the furnace temperature of 890°C. The specimen temperature calculated from Eq. (1) must be overestimated, but this analysis leads to a significant conclusion regarding the flash event and the temperature of the specimen in the damaged area.

\[ \Delta T = \frac{W}{4\sigma a T_0^3} \]

(1)

The current surge at the onset of the flash event is likely to occur by an n-type electric conduction.

The oxygen anion’s diffusivity at the grain boundaries is significantly higher than that in the grain interior of the BaTiO$_3$. The oxygen reduction rate at the grain boundaries should be determined by the grain orientation relationship, i.e., randomness of atomic configuration at the grain boundaries. Because the electron carriers’ density is increased with the increasing oxygen vacancies, the grain boundaries with high coherency should have a lower electric conductivity than the random boundaries. The electric current preferably goes through the random grain boundaries with a low resistivity, and hence the temperature of the random grain boundaries increases due to Joule heating, resulting in the formation of the second phase layers along the grain boundaries. The flash event in BaTiO$_3$ is probably triggered by an n-type conduction along the random grain boundaries where the electric conduction selectively occurred.

5. Conclusion

Fully densified BaTiO$_3$ polycrystals showed a flash event at 890°C under the DC field of 133 V/cm; the electric current of the specimen abruptly increased at the furnace temperature. After the flash event, tunnellike damage was created through the specimen between the Pt electrodes. Formation of the grain boundary second layers in the damaged area was confirmed by TEM and HRTEM observation, though more than half of the grain boundaries in the vicinity of the damaged area were free from the second phase layers. The grain boundary second phase layer was a crystalline phase with a low Ba/Ti atomic ratio. The specimen temperature estimated from the electric power dissipation at the onset of flash was 1891°C, which is significantly higher than the furnace temperature. The temperature in some grain boundaries increased by Joule heating during the flash event, and hence the chemical composition in the vicinity of the grain boundaries changed due to vaporization of the Ba cations. The second phase layers were consequently created along the grain boundaries where the electric conduction selectively occurred during the flash event.

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