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Oxygen vacancy formation due to DC electric fields during flash sintering in $BaTiO_3$

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A unique sintering technique called *FLASH sintering* has been developed by Raj's research group[1)]. When green compacts are heated under DC electric fields beyond threshold strength, specimen current abruptly increases at a critical temperature, and then densification is immediately completed at very short time. The sintering temperature and time largely decrease with the increasing DC electric fields. Cologna *et al*. successfully obtained fully densified YSZ at 850°C for 5s at 120V/cm without any outer pressure. After their reports, flash sintering has been applied for various kinds of ceramic materials such as Y_2O_3, Al_2O_3, $CoMnO_4$, and so on. To obtain fully sintered compacts by flash sintering, it is very important to input electric power into the green compacts effectively during the flash event. However, in $BaTiO_3$, dielectric break down occurs under critical field strength. This is different from the other ceramics described above[2)]. The dielectric break down results in the formation of damaged structure such as holes and so on. The dielectric break down is related to the steep increase of spaceman electric current during the flash event. However, the detailed mechanism of the steep increment of the spaceman electric current has not been clarified yet. In this study, STEM, EDS and EELS analysis was performed in flash sintered $BaTiO_3$ to reveal the microstructure of the dielectric break down paths and to determine the defect structure at grain boundaries in high-purity $BaTiO_3$.

$BaTiO_3$ sintered bodies were prepared from commercially available $BaTiO_3$ powders (99.9%, Ba/Ti=1.000, 0.1μm). Green compacts with the dimension of 15×5×5mm^3 were set in a dilatometer modified to apply electric fields, and conducted flash sintering experiments. The specimen current was precisely controlled, and shrinkage rate and specimen current were monitored during the sintering experiments. After the flash event, the microstructure was analyzed by Cs-corrected STEM (ARM-200FC).

It was confirmed that flash sintering effectively increases sintering rates in $BaTiO_3$. For example, the sintered compact with the relative density more than 90% was obtained at 1020°C for 1min at the applied field of 100V/cm. However, the final density decreased, and several discharging holes appeared at the field strength beyond a critical value. After discharging, second phases are formed in the damaged portion near the discharging holes. A typical secondary phase formed at the damaged portion is shown in Figure 1. The secondary phases as indicated by the arrow A are always formed at grain boundaries due to the flow of large current. The secondary phases have Ti-excess composition, suggesting that grain boundaries partially melted and a part of Ba vaporized during the flash event. The secondary phases were found to be preferentially formed through incoherent grain boundaries. As shown in Fig. 1, a grain boundary on the opposite side of the secondary phase has no secondary phase as indicated by the arrow B in the image. On the other hand, EELS analysis has revealed that excess oxygen vacancies are formed in the area apart from the damaged portion during the flash event. This fact indicates that the generation of oxygen vacancies is accelerated by the application of DC electric fields. In addition, the excess oxygen vacancies were found to retard the shrinkage rate at a final sintering stage.

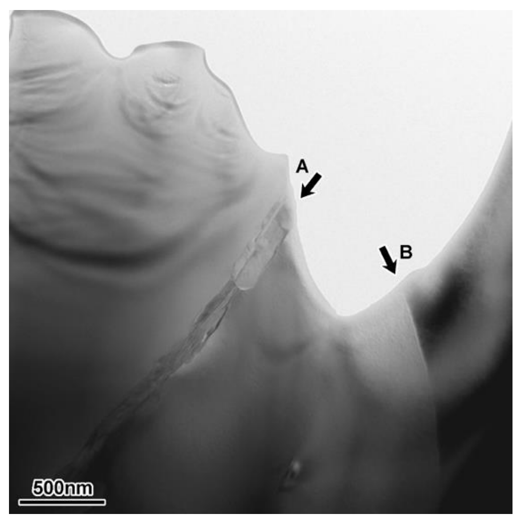

Figure 1 TEM bright field image showing secondary phase due to discharging in $BaTiO_3$.

1) M. Cologna, B. Rashkova and R. Raj, *J. Am. Ceram. Soc*., **93**, 3556 (2010).
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