Enhancement of sintering rates in BaTiO₃ by controlling of DC electric current

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Abstract

DC electric fields ranged from 25 to 350 V/cm enhanced the sintering rates of BaTiO₃. At the field of 25 V/cm, the sintering densification occurred by field-assisted sintering (FAST), and flash-sintering preceded by FAST was observed at the field strength of more than 75 V/cm. Most of the densification, however, was produced by the FAST process. At high field strength of more than 250 V/cm, the sintering densification was not finished owing to discharging during the flash-sintering. By means of FAST process at 100 V/cm and the current limit of 100 mA, in contrast, relative density of 97% and a fine grain size about 500 nm were achieved at 1020°C in the present material. The FAST process, where the electric current was set to the transition current between FAST and flash-sintering, is highly effective to fabricate uniform and fine grained BaTiO₃ polycrystal.

Key-words : Flash sintering, BaTiO₃, Sintering, Fast, HRTEM

1. Introduction

It has been widely accepted that application of electric fields during sintering facilitates densification of ceramics. For instance, direct current (DC) electric field of 20 V/cm lowers the sintering temperature of 3 mol% Y₂O₃-stabilized tetragonal ZrO₂ polycrystal (3Y-TZP) from 1500°C to around 1300°C. The enhancement of sintering by electrical fields has been explained in terms of suppressed grain growth during sintering. The sintering techniques using electric fields are collectively categorized as field assisted sintering (FAST). Sintering densification of ceramics is gradually accelerated by FAST. More recently, Raj et al. have found flash-sintering phenomenon, where densification occurs almost immediately (typically <5 s) under higher electric fields. 3Y-TZP can be fully densified even at 850°C for 5 s under an electric field of 60 V/cm nevertheless the sintering temperature generally used for 3Y-TZP is around 1500°C for a few hours. Flash-sintering has been demonstrated mainly by Raj’s research group in various ceramics including cubic zirconia, cobalt manganese oxide (Co₂MnO₄), Mg-doped alumina (Al₂O₃), strontium titanate (SrTiO₃), ytria (Y₂O₃), TiO₂ and BaTiO₃. Nearly full density could be achieved at lower sintering temperature for very short time in all of the demonstrated ceramics.

Abrupt densification in flash-sintering is always accompanied by steep increment of specimen current. Under critical temperature and field strength, drastic increment of current occurs, resulting in significant Joule heating. Generally, electrical conductivity in insulating ceramics increases with the increasing temperature. However, the drastic increment of current observed in flash event can be hardly explained from thermal activation of charge carriers across a band gap. According to the previous investigations, it would seem that the formation of point defects such as Frenkel type defects under electric fields contributes to the surge of current and mass transport, resulting in the flash-sintering. At the onset of the drastic increment of the current, a trigger point must exist and an initial electric path must be related to the instability of electrical conductivity against temperature and electric field. The instability of the electrical conductivity presumably leads to ununiform microstructure in flash-sintered body. The instability effect to the formation of microstructure would become remarkable in ceramics such as BaTiO₃ because the temperature dependency of the electrical conductivity is higher due to large oxygen nonstoichiometry. Actually, M’Peko et al. recently reported that BaTiO₃ exhibits discharging inside the compacts during flash event over a critical electric field and current. Meanwhile, according to the previous studies on flash-sintering, Yoshida et al. has suggested that FAST process followed by flash event significantly contributes to densification in dielectric ceramics such as Y₂O₃ and Mg-doped Al₂O₃. Here, in this study, FAST process is defined as the sintering process where current gradually increases. After the gradual increment, the current abruptly increases, i.e., flash-sintering event. Grain growth rates as well as sintering rates change in the two sintering process of FAST and flash-sintering. To avoid the instability of the current flow and to obtain fine grained structure, a ratio of FAST and flash-sintering must be a crucial factor to fabricate fully-densified ceramics such as BaTiO₃.

In this study we demonstrate that DC fields greater than 75 V/cm can trigger the flash-sintering in undoped BaTiO₃, which is widely used for electro-ceramics whose electrical conductivity is sensitive to oxygen nonstoichiometry at elevated temperatures. It is noteworthy that the FAST process is highly effective to fabricate uniform and fine grained BaTiO₃ polycrystal.

2. Experimental

Commercially available BaTiO₃ powders (SAKAI chemical...
industry Co., Ltd., purity >99.9%, Lot. No. 1308607) were used for sintering. An initial particle size and Ba/Ti ratio of the powders is 0.1 μm and 1.000 according to a manufacturing report. The sintering temperature required for full densification in the present material is 1350°C by conventional sintering, and the typical grain size in the sintered body is about 20 μm.

The raw powders were uniaxially pressed at 30 MPa with a cemented carbide die into a rectangular shape, and further cold isostatically pressed under a pressure of 100 MPa. The dimensions of the green compacts were 10 mm in width, 30 mm in length and 2 mm in thickness. After that, two holes with the diameter of 1.5 mm were machined about 5 mm inside from both sides of the green compacts. The distance between the respective holes was 20 mm. Pt wires with the diameter of 0.3 mm was fixed at the respective holes with Pt paste. The specimen was suspended by the Pt wires inside a box type furnace. A DC field ranged from 25 to 350 V/cm was applied through the Pt wires by a stabilized power supply (HEP-3 2100, Matsusada Precision Inc.), and current limit was set to 500 mA at the power supply. The specimen was heated in air from room temperature up to 1300°C at a constant rate of 300°C/h. When the specimen current reached at the limited value, the furnace temperature and voltage were kept for 1 min, and then, the furnace and the applied voltage were switched off. In order to examine an effect of FAST on BaTiO3, the sintering experiments at 75 and 100 V/cm were separately performed at the current up to 130 and 100 mA, respectively; just before the occurrence of the surge of electric current and flash-sintering, the furnace temperature and current were immediately turned off. After the sintering experiments, linear shrinkages of the sintered specimens were determined by measuring the distance between the two holes. For comparison, the shrinkage behavior of the green compact without electric fields (i.e., conventional sintering) was measured by dilatometry.

The microstructures of the sintered compacts were observed by SEM (S-3000, Hitachi High-Technologies Corp.) and HRTEM (ARM-200F, JEOL Ltd.). A center area of fractured surfaces was used for SEM observation. Thin foils for TEM observations were prepared by a conventional procedure including Ar ion milling.

3. Results and discussion

Figure 1 shows a plot of specimen currents as a function of furnace temperature. The inset is a plot of input electric powers of the respective specimen during sintering. At 25 V/cm, the specimen current exhibits gradual increment at temperatures examined in this study. At higher electric field, in contrast, the current increased with the increasing furnace temperature and then abruptly increased up to the current limit at critical temperatures. The onset temperature of the abrupt increase in current was about 1100°C at 75 V/cm and 800°C at 250 V/cm, respectively. The steep increment in current indicates the occurrence of flash event. On the other hand, the regime where the current gradually increased must correspond to FAST. The FAST regime is shortened with increasing applied electric field; the transition currents from FAST to flash event decreases with increasing applied electric field, as indicated by the arrows in the plot. These behaviors of the specimen current during sintering are similar to those of previous reports obtained from other materials such as zirconia, Y2O3 and TiO2. The plot of input power suggests that the transition from FAST to flash took place at critical power of about 20 W as indicated by the dotted line. The same trend was also found in other materials.

The final linear shrinkages after the FAST (at 25 V/cm) and flash-sintering (at >75 V/cm) are plotted in Fig. 2 with filled triangles and circles, respectively. For comparison, linear shrinkage curve of BaTiO3 without electric field is also shown in Fig. 2. In the conventional sintering without electric field, densification began around 800°C, and the linear shrinkage of 17% (the relative density of 97%) was achieved at 1400°C. In contrast, the linear shrinkages of the sintered specimens are always higher than that of the conventionally sintered body at the corresponding temperatures. For example, the linear shrinkage of 14.8% was obtained at 1020°C under the electric field of 100 V/cm, while only 5% was achieved in the conventionally sintered material at the same temperature. The application of high electric field is effective to improve the sinterability of BaTiO3. However, final densities of the flash sintered bodies were lower than 90% at the field strength beyond 75 V/cm, while the relative density of 98% was obtained by FAST at the field of 25 V/cm. The effectiveness of electric field to sinterability obtained in this study is similar to that reported by M’Peko et al.

In order to examine the effect of FAST process on the densification, the sintering experiments until the occurrence of flash event were separately performed; the sintering experiments at 75 and 100 V/cm were quitted just before the occurrence of the
flash event at the current of 130 and 100 mA, respectively. The linear shrinkage data obtained only by FAST at 75 and 100 V/cm are shown by open triangles in Fig. 2. It is noted that the FAST process contributes to significant portion of the total shrinkages in comparison with the flash-sintering; the shrinkage given by FAST is more than 90% of the total shrinkage at 100 V/cm, and the relative density of 98% was achieved only by FAST at 25 V/cm. The large contribution of the FAST process to the total shrinkage is also reported in Y2O3.9) In case of Y2O3, a ratio of the contribution of FAST to the total shrinkage is increased with the decreasing applied fields. However, the electric field dependency of a total shrinkage is very different between BaTiO3 and Y2O3; full densification was not achieved only by the flash-sintering at higher electric fields of 250 and 350 V/cm, while almost full densification can be obtained only by the flash-sintering in Y2O3.9) The total shrinkage in the present material decreases with increasing applied electric fields as seen in Fig. 2. This result indicates that the FAST is much effective for densification of BaTiO3 in comparison to the flash-sintering process.

The occurrence of discharging reported by M’Peko et al. is also confirmed in this study.11) Figure 3 shows a set of micrographs taken from flash-sintered compact at 100 V/cm. The optical image (a) and SEM image (b) were taken from a fractured surface of the sintered body. The fracture surface was perpendicular to the applied field and current. As seen in the images, a hole exists inside the compact after flash-sintering, indicating that discharge occurred during flash event. The grains around the hole are confirmed to exhibit rapid growth as shown in the image (c). This fact suggests that input electric power did not contribute effectively to the densification owing to the discharge. This situation is quite different from the case of other ceramics. The limited densification at high field strength beyond 250 V/cm is likely to result from the discharge. The criterion to discharging is roughly coincident to the results obtained by M’Peko et al.11) In contrast, grains are very uniform apart from the damaged area. In the area, neither secondary phase nor amorphous layer was observed as directly confirmed in TEM images (d) and (e).

It has been demonstrated that the flash-sintering under high electric fields is very effective to lower the sintering temperature and to accelerate the densification rate. In the case of BaTiO3, however, the flash-sintering under high fields results in low density and inhomogeneous microstructure due to the discharge. In contrast, FAST process is preferable for obtaining uniform and fine grained structure in BaTiO3 as shown in Figs. 3(d) and 3(e). To accelerate the densification rate effectively, it would be better to control the current at maximum in FAST process. In order to demonstrate the effectiveness of FAST process on BaTiO3, the FAST process was kept at a critical current just below the transition point from FAST to flash event by precisely controlling the specimen electric current, for 30 min at 100 V/cm; the sintering experiment was performed at 100 V/cm up to 100 mA and 1020°C, and then the current and furnace temperature were kept for 0.5 h. Here, the current of 100 mA is just below the critical current where flash event occurs. Figure 4 shows (a) SEM and (b) HRTEM images taken from the sintered compact. Very fine grained and uniform structure could be obtained as shown in the image of Fig. 4(a). A grain size is about 500 nm. In addition, grain boundaries are free from any secondary phases and precipitate as seen in HRTEM image showing the area including a grain boundary. The final linear shrinkage obtained by the FAST with 30 min duration is shown in Fig. 2 by the filled square. The sintered specimen exhibited the relative density of 97% for short time of 30 min. To control the specimen current precisely just below the critical current of flash event, densified compact with uniform and fine grained structure could be successfully obtained.

BaTiO3 has oxygen nonstoichiometry defined as BaTiO3-x, where the electrical conductivity is n-type at δ > 0 and p-type at δ < 0, resulting in higher electrical conductivity at elevated temperatures.12),13) At onset of flash event, a locally heated portion would appear to form an instability path of electric current, when additional Joule heating occurs at the local portion. At this time, the steep increment of the electric current tends to be localized around the initial path because the electrical conductivity becomes larger there due to the high temperature dependency of the electrical conductivity in BaTiO3-x. The characteristic behavior of the electric path formation results in a trigger of the discharge observed in the present study. The instability of the electric path formation is remarkable in the materials exhibiting higher temperature dependency of the electrical conductivity. In such materials, it would be better to control a ratio of FAST/flash-sintering by tuning the current carefully. Meanwhile, Shikhar et al. investigated electric field dependency of grain sizes in compacts sintered by FAST and/or flash-sintering.10) According to their results, a grain size initially increases to show maximum, and decreases to show minimum and exhibits gradual increment with increasing electric fields. The detail mechanism of the electric field dependency of grain sizes has not been clarified yet by them.10) The grain size exhibits a tendency to increase in flash-sintering regime. This fact means that electric fields should
be decreased to obtain fine grained structure, suggesting to a transition point between FAST and flash event. At the transition point, a grain size would become at a minimum size as described in the result showing the electric filed dependency of grain sizes. A technique of controlling the current precisely at the transition current between FAST and flash event can be considered to be an effective way to lower sintering temperature, time and to obtain uniform fine grained structure.

4. Conclusions

In summary, the sinterability of BaTiO₃ was improved by the application of electric fields. At the field strength of more than 75 V/cm, the surge of electric current, which indicated the occurrence of flash event, was observed in the present material. However, most of the densification is produced during the FAST process. At high voltage beyond 250 V/cm, the discharging probably suppressed full densification during flash-sintering. By means of the FAST process by controlling the specimen electric current for 30 min at 100 V/cm just below a critical current of flash event, BaTiO₃ compacts with the relative density of 97% and the grain size about 500 nm was obtained only at 1020°C.

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References