Suppression of Abnormal Grain Growth in Barium Titanate by Atmosphere Control

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Abstract The ferroelectric properties of barium titanate strongly depend on its microstructure, in particular, grain size and distribution. During sintering, $BaTiO_3$ usually exhibits abnormal grain growth, which deteriorates considerably the ferroelectric properties. A typical technique to suppress the abnormal grain growth is the addition of dopants. Dopant addition, however, affects the ferroelectric properties and thus limits the application of $BaTiO_3$. Here, we report a simple but novel technique to prevent the abnormal grain growth of $BaTiO_3$ and to overcome the limitation of dopant use. The technique consists of stepwise sintering in a reducing atmosphere and in an oxidizing atmosphere. The materials prepared by the present technique exhibit uniform grain size and high dielectric properties. The technique should provide opportunities of having $BaTiO_3$-based materials with superior ferroelectric properties.

1. Introduction

Barium titanate is an essential material for the modern electronic components industry. It is used for the multilayer capacitor, positive temperature coefficient (PTC) resistor, grain-boundary barrier layer capacitor (BLC), etc.[1-4] To maximize the electrical properties of these electronic components, their microstructures have to be optimized during processing.[5-7] In general, the desired microstructure is grains of small and uniform size on the order of a micron. However, abnormal growth of some grains usually occurs in fine matrix grains unless the powder is very carefully prepared to have a stoichiometric composition or is heavily doped with some specific dopants, for example, La^{3+} and Nb^{5+} ions.[8-12] When the powder is stoichiometric or Ti-deficient, the abnormal grain growth does not occur; however, densification of powder compacts is very difficult.[13] Powders with TiO_2-excess

compositions are usually used to enhance the densification.[14-15] In pressureless sintering, dopant addition has been the only means for suppressing abnormal grain growth while retaining a high sinterability of compacts with excess TiO_2.[8-12,16] Dopant addition, however, affects and limits the ferroelectric properties of the material. It is thus desirable to control the abnormal grain growth of $BaTiO_3$ regardless of the addition of dopants.

Our recent investigations[17-19] on the microstructure development in $BaTiO_3$ showed that a reducing atmosphere suppressed the growth of preexisting large abnormal grains with {111} twins and further the formation of {111} twins during sintering at temperatures below the eutectic temperature of 1332°C. These results suggest that a reducing atmosphere can totally suppress the abnormal grain growth in $BaTiO_3$ and result in a fine and uniform microstructure. The purpose of the present investigation is to demonstrate an

experimental technique to suppress the abnormal grain growth and to improve the dielectric properties without using a dopant.

2. Experimental procedure

We prepared $BaTiO_3$ samples with various amounts of TiO_2 addition using commercial $BaTiO_3$ powder (HPBT-1 Fujititanium, Kanagawa, Japan) and TiO_2 (Aldrich Chem. Com., Milwaukee, WI, USA) powder. The purities of the $BaTiO_3$ and TiO_2 powders were 99.8 and 99.9 wt%, respectively, and their size was ~0.3 μm. The proportioned powder was ball-milled using a polyethylene bottle and zirconia balls. The dried slurry was crushed and isostatically pressed into disks with a diameter of ~8 mm and a thickness of ~4 mm under 200 MPa. For microstructure observation, the powder compacts were sintered at 1250°C either in air or in $95N_2$-$5H_2$ ($P_{O_2} = 10^{-15} \sim 10^{-20}$) atmosphere for up to 100 h. Some $95N_2$-$5H_2$-sintered compacts were further annealed at 1350°C for 5 h in air to observe the microstructure change with oxygen annealing above the eutectic temperature. For dielectric property measurement, 0.4-mol%-TiO_2-added powder compacts were sintered at 1250°C-1350°C either in air or in H_2 for 5 h. Since the H_2-sintered samples are semiconductive, the samples were air-annealed at 1350°C for 5 h to regain their dielectric properties. The microstructures of the samples were observed using a scanning electron microscope (SEM) and a transmission electron microscope (TEM). For the SEM observation, the samples were polished and etched in a $95H_2O$-$5HCl$ (vol%) solution. The dielectric constant was measured using an impedance-gain phase analyzer.

3. Results and discussion

Figure 1 shows the two types of microstructures obtained after the sintering at 1250°C, a temperature
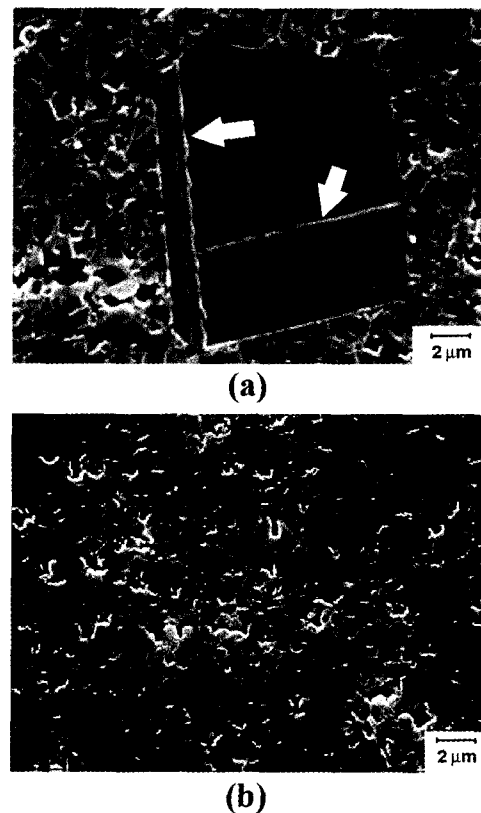

(a)

(b)

Fig. 1. SEM micrographs showing the microstructures of $BaTiO_3$ samples with 0.4-mol%-TiO_2 addition sintered at 1250°C for 10 h (a) in air and (b) in $95N_2$-$5H_2$.

below the eutectic temperature of 1332°C: one with abnormal grains (Fig. 1a), and the other without abnormal grains (Fig. 1b). All the samples sintered in the reducing atmosphere ($95N_2$-$5H_2$) showed microstructures similar to those of Fig. 1b. On the other hand, all the samples, except the sample without TiO_2 addition, sintered in an oxidizing atmosphere (air) showed microstructures similar to those of Fig. 1a.

In all the samples, almost all the abnormal grains examined (~200 grains) contained {111} twins, in particular, double twins (indicated by arrows in Fig. 1a) as in previous investigations,[20-21] while the fine grains rarely contained {111} twins (Fig. 1). In addition, the number of abnormal grains per unit area in the samples sintered in air increased
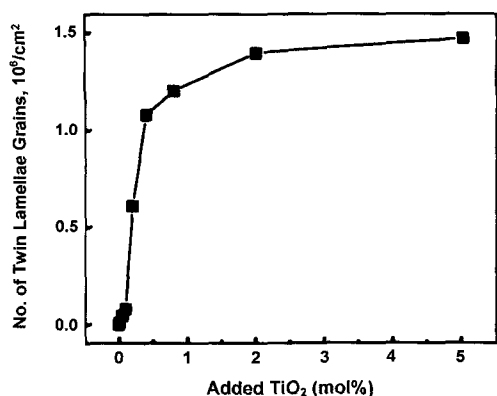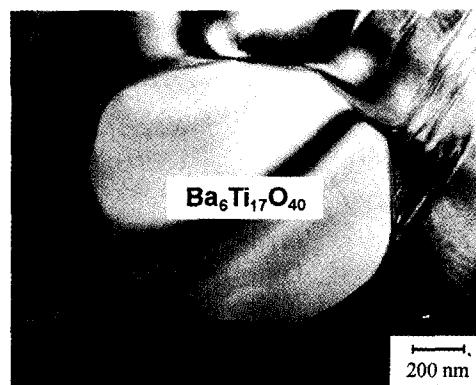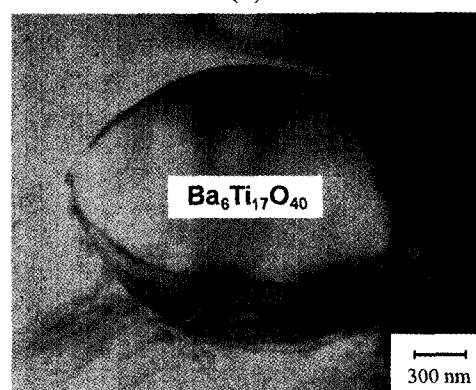
Fig. 2. Increase in the number of the grains containing twin lamellae with TiO_2 addition.

(a)

(b)

Fig. 3. TEM micrographs showing the shape of $Ba_6Ti_{17}O_{40}$ particles trapped in $BaTiO_3$ grains sintered at 1250°C (a) in air for 200 h and then (b) in $95N_2$-$5H_2$ for 100 h.

with increased additions of TiO_2, as shown in Fig. 2. This suggests that the formation of abnormal grains is related to both an excess of TiO_2 and an oxidizing atmosphere and can be prevented by sintering the sample in a reducing atmosphere.[18-19]

In the $BaTiO_3$-TiO_2 system in air, excess TiO_2 forms a $Ba_6Ti_{17}O_{40}$ phase below the eutectic temperature of 1332°C.[22] A WDS analysis of the second phase particles in the sintered samples revealed that the Ba to Ti ratio was 6:17, irrespective of the sintering atmosphere, either air or $95N_2$-$5H_2$. To identify the crystallographic structures of the second phase particles, we prepared a $25BaCO_3$-$69TiO_2$ (molar ratio) powder mixture and calcined it at 1150°C for 100 h in air to make a $20BaTiO_3$-$80Ba_6Ti_{17}O_{40}$ mixture. The calcined powder was isostatically pressed and then sintered at 1250°C for 100 h in either air or $95N_2$-$5H_2$. The X-ray diffraction analysis revealed that the phases were $BaTiO_3$ and $Ba_6Ti_{17}O_{40}$ irrespective of the sintering atmosphere, but the crystal structures of $Ba_6Ti_{17}O_{40}$ were different in different atmospheres. Both were monoclinics but with a space group A2/a in air and a space group C in $95N_2$-$5H_2$; this is in agreement with a previous report.[23] Not only the crystal structure but also the interface morphology of

the $Ba_6Ti_{17}O_{40}$ particles differed according to the sintering atmosphere. The transmission electron micrographs in Fig. 3 show that the interface of $Ba_6Ti_{17}O_{40}$ is faceted in air and is rough (defaceted) in $95N_2$-$5H_2$. Similar faceted and rough $BaTiO_3$ grain boundaries in air and $95N_2$-$5H_2$, respectively, were previously observed.[17]

The present microstructural observation suggests that the {111} twin formation and the grain growth behavior in $BaTiO_3$ are related to the interface morphology in the $BaTiO_3$ sample. When the interfaces are faceted with a high energy anisotropy in an oxidizing atmosphere, the {111} twins form in the presence of a $Ba_6Ti_{17}O_{40}$

phase. Once the {111} twin lamellae form, the twin lamellae can induce abnormal grain growth in the oxidizing atmosphere. In contrast, when the interfaces are rough in a reducing atmosphere, {111} twins do not form even in the presence of a $Ba_6Ti_{17}O_{40}$ phase and the abnormal grain growth is totally suppressed.

The benefit of sintering in a reducing atmosphere for dielectric properties is shown in the following example. 0.4-mol%-TiO_2-added $BaTiO_3$ powder compacts were first sintered at 1250°C for 5 h in H_2 to obtain a uniform and fine microstructure with a 1.5 μm average grain size and then annealed at 1250°C or 1350°C for 8 h in air to oxidize the sintered samples. During the air-annealing, the sample oxidizes in a short time, less than a hour, because of relatively fast oxygen diffusion in $BaTiO_3$.[24] The air-annealing up to 100 h at 1250°C or 1350°C, however, did not induce any abnormal grain growth. The air-annealing just increased the average grain size from 1.5 μm to a maximum of 2.0 μm. This result shows that once the abnormal grain growth is inhibited in a

reducing atmosphere below the eutectic temperature, further sintering or annealing in an oxidizing atmosphere may not cause any abnormal grain growth at any temperature, below or above the eutectic tem-perature.

Figure 4 plots the temperature dependence of the effective dielectric constant for the H_2-sintered samples annealed at 1250°C or 1350°C for 2 h in air together with that of the sample sintered at 1350°C for 2 h in air. The effective dielectric constants of the H_2-sintered and air-annealed samples are much higher than that of the just air-sintered sample: at room temperature, the effective dielectric constant is ~4000 for the former and ~1700 for the latter. The air-sintered sample contained many abnormal grains in the fine matrix, similar to that in Fig. 1a.

4. Conclusions

We developed a new processing technique of $BaTiO_3$ which ensures a fine and uniform microstructure and high dielectric properties. The technique is simply sintering in a reducing atmosphere and then annealing in an oxidizing atmosphere. Sintering in a reducing atmosphere totally suppressed the {111} twin formation and abnormal grain growth of $BaTiO_3$ because of the rough interface of $Ba_6Ti_{17}O_{40}$ and also the rough grain boundary of $BaTiO_3$ in the reducing atmosphere. The fine microstructure obtained after the reducing-atmosphere sintering was retained during further annealing in an oxidizing atmosphere; this allows to maximize the dielectric properties of the sample. The stepwise sintering-and-annealing technique in a reducing and an oxidizing atmosphere should be applicable in the preparation of $BaTiO_3$-based materials with superior electrical properties.
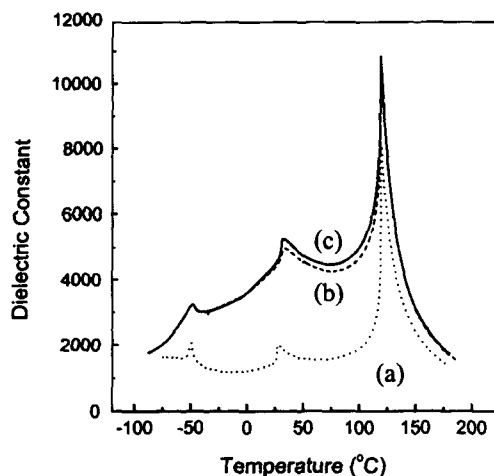
Fig. 4. Variations of dielectric constants with measuring temperature of the 0.4-mol%-TiO_2-added $BaTiO_3$ samples (a) sintered at 1350°C for 2 h in air, (b) sintered at 1250°C for 5 h in H_2 and annealed at 1350°C for 2 h in air, and (c) sintered at 1250°C for 5 h in H_2 and annealed at 1250°C for 2 h in air.

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