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Fabrication and characteristics of fine-grained $BaTiO_3$ ceramics by spark plasma sintering

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Abstract

Fine-grained $BaTiO_3$ ceramics were obtained at a low sintering temperature of 900 °C within a short sintering period by means of a new sintering method-spark plasma sintering (SPS). The ceramics are highly densified to more than 99% of the theoretical X-ray density with homogeneous microstructures, signifying that the SPS process is effective for the densifying of compacts and the inhibition of exaggerated grain growth. Nanocrystalline $BaTiO_3$ powder of 13 nm grain size was used as the starting material. Observations of pellets by HRTEM indicated that the grains only support 180° domain structures and in some cases unusual twins were discovered. XRD measurement shows that in fine-grained SPS pellets a small amount of cubic phase is present. A clear dependence of the dielectric constant on grain size was observed. It is believed that the existence of twins is one of the key factors that resulted in the slight decrease of the dielectric constant of fine-grained ceramics.

Keywords: B. Grain size; C. Dielectric properties; D. Barium titanate; Spark plasma sintering; Nanostructured materials

1. Introduction

$BaTiO_3$ is a ceramic material with superior ferroelectric properties that has found widespread application in the manufacture of multilayer capacitors, thermistors, sensors, actuators and electronic components [1–3]. Recently, based on the requirement for high precision, high reliability and miniaturized electronic components, the grain size effect on dielectric properties of fine-grained ferroelectrics has attracted much attention [4–7]. Due to difficulties in preparing dense $BaTiO_3$ ceramics with fine grains via conventional sintering processes, few reports on the fabrication of fine-grained $BaTiO_3$ ceramics have been found. It is a clear target for researchers to obtain dense fine-structured ceramics and study their properties [8]. It is noted that the consolidation of a starting nanopowder is complicated because of the presence of a high surface area, high levels of chemisorbed gases, and interparticle friction effects. But even if all these problems have been solved, sintering of green compacts can involve exaggerated grain growth. Some additives have been reported to effectively prevent discontinuous grain growth [9–11], but when physical property requirements are the most stringent, these additives should be avoided. Thus unless grain growth during sintering can be controlled, the prospects for producing dense ceramics consisting of fine grains are slim.

In the traditional sintering procedure [12], a temperature of about 1300 °C must be achieved and maintained for 1 h or longer. The resulting ceramics usually demonstrate a grain size at the micrometer level. Oonishi et al. [13] fabricated dense $BaTiO_3$ ceramics (above 98% relative density, R.D.) with submicrometer grains (0.2–0.6 μm) by hot isostatic pressing (HIP). A pressure of 500 MPa was applied to the powder at 800 °C. As described in this paper, we prepared high-density, fine-grained $BaTiO_3$ ceramics at the much lower temperature of 900 °C and at short sintering periods of some minutes by the Spark Plasma Sintering (SPS) method. It is concluded that the short sintering period is advantageous in suppressing exaggerated grain growth. The sintering properties, microstructures and dielectric

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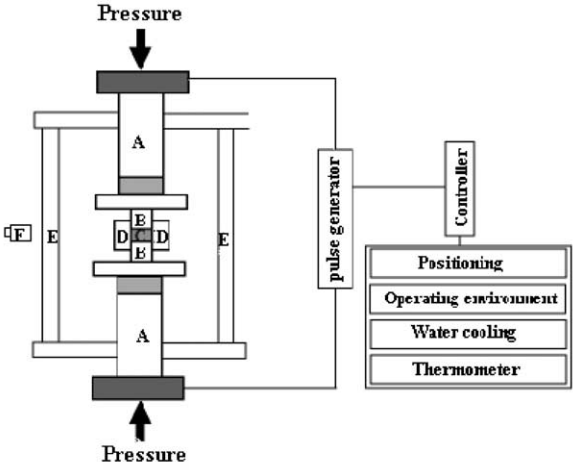
properties are examined and compared with those resulting from the conventional sintering method.

2. Experimental procedure

The starting powder was fabricated by the following sol–gel method. Barium oxyhydrate and tetrabutyl titanate were separately dissolved in ethylene glycol monomethyl ether and ethanol. These two solutions were then mixed and stirred to form a clear sol containing barium and titanium in a ratio of 1:1. Then water-diluted ethylene glycol monomethyl ether was slowly added to the sol. A few minutes later, a homogeneous gel was obtained. After being oven-dried and ground, the gel was heat-treated at 600 °C to obtain crystalline $BaTiO_3$ powder. The average grain size of as-prepared powder was determined by transmission electron microscopy (TEM) to be 13 nm with a BET value of 33 m^2/g, meaning the precursor powder is agglomerated, which is hard to avoid in the sol–gel method.

In the spark plasma sintering (SPS) process, the chemically homogenous powder was poured into a graphite die and sintered at a heating rate of 200 °C/min. A pressure of 50 MPa was applied at the beginning of the sintering process and was released during the cooling part of a complete sintering cycle. The pulse duration time was set as 3.3 ms and one pulse sequence contained 12 pulses with average interval of 6.6 ms. A high pulse sequence current of 3000 A was utilized. The sintering temperature was monitored by a conventional thermocouple (K type) up to 1000 °C. Above 1000 °C, a digital radiation thermometer was used. Both of the above mentioned methods are applied to the side of the graphite die.

After SPS sintering, the pellets were annealed in air to remove the carbon contamination. As-sintered samples (20 mm in diameter) are referred to here as SPS pellets. Meanwhile, for the conventional sintering process, the same powder was pressed into pellets without a binder, followed by cold-isostatic pressing at 400 MPa. These green bodies were sintered in air for 2 h, and are called CIP pellets. The densities of all the samples were measured using Archimedes' method in water. X-ray diffraction analysis was carried out to determine phase structure. For SEM investigation, the pellets were hot-etched at temperatures according to their sintering processes. To observe the microstructure of SPS pellets, samples were thinned to about 0.05 μm using ion-beam etching. The dielectric properties of ceramics were determined with an HP4192A impedance analyzer at a frequency of 1 kHz during the heating process from RT to 200 °C at 3 °C/min.



A: Punch Electrode B: Punch C: Sample D: Graphite die
E: Vacuum and water cooling chamber F: Optical pyrometer

Fig. 1. Schematic diagram of the spark plasma sintering (SPS) system.

3. Results and discussion

3.1. Sintering properties

The SPS system shows high heat efficiency besides the virtues of hot-pressed sintering. It produces a high temperature field by means of pulse energy, spark pulse pressure and Joule heating. Instead of heating by an external source, a pulsed DC current is applied, which passes through the pressure die as well as the sample, so that the sample is heated both from outside and inside. For each grain interior, the specimens are self-heated and the surfaces of grains are simultaneously excited by spark plasma, which is suddenly generated during the process of SPS. All of these processes promote materials transfer and enhance the densification.

Fig. 1 demonstrates the schematic of spark plasma sintering. The SPS system is commonly used in producing metal and engineering ceramics [14], there are relatively few researchers who have investigated the technique for oxides. It is found that this process is advantageous in producing fine-grained ceramics by suppressing exaggerated grain growth [15].

The densities of SPS pellets are plotted as a function of sintering temperature in Fig. 2, compared with that of CIP pellets. High-densified pellets (more than 94% R.D.) were obtained when sintered at a much lower temperature of 750 °C for 3 min by the SPS method. At 900 °C, almost fully-dense ceramics (above 99% R.D.) can be achieved. On the other hand, CIP pellets showed much lower densities than the SPS pellets, even when sintered at 1250 °C, which is more than 300 °C higher than the SPS method. Moreover, the sintering period of the SPS process is extremely short. It only took 3 min at the highest temperature to complete this procedure. The dependence of density on hold time is shown in Fig. 3. When shortening the holding time from 3 to 1 min at 900 °C or a holding time of zero minutes near 900 °C, the

densities reduced from 99.2 to 97.4 and 96.2%, respectively. It can be inferred that even without a holding time, the pellets can still be sintered to high density.

3.2. Microstructure and phase structure

A typical SEM micrograph of hot-etched and TEM micrograph of ion-thinned surfaces of SPS pellets sintered at 900 °C without hold time are shown in Fig. 4(a) and (b). As a comparison, a micrograph of a CIP pellet is given in Fig. 4(c). The SPS pellets consisted of mainly submicrometer grains of 200 nm and some domains can be clearly observed. With the lengthening of the hold time, larger grain size was found, namely 340 and 730 nm for 1 and 3 min hold periods. Experiments have also been performed expanding the hold time to 30 min; and an exaggerated grain growth was observed and a grain size of about 3 μm was obtained. These results indicate that the short sintering period is an essential factor to obtain fine-grained $BaTiO_3$ ceramics by the SPS process. In contrast to SPS pellets, the average grain-size of the CIP pellets sintered at 1250 °C for 2 h is much larger (more than 2 μm) and the microstructure is more inhomogeneous than that of SPS pellets.

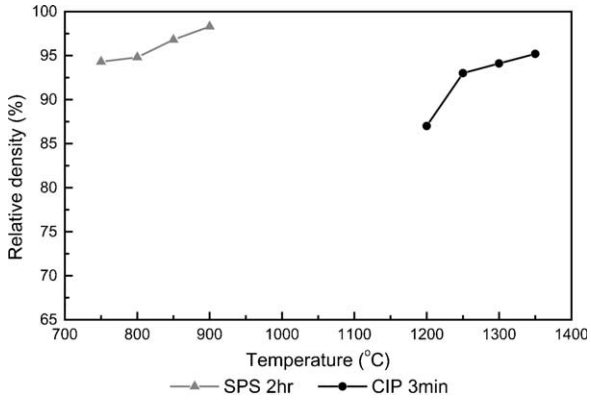


Fig. 2. Comparison of relative density between SPS and CIP pellets as a function of sintering temperature.

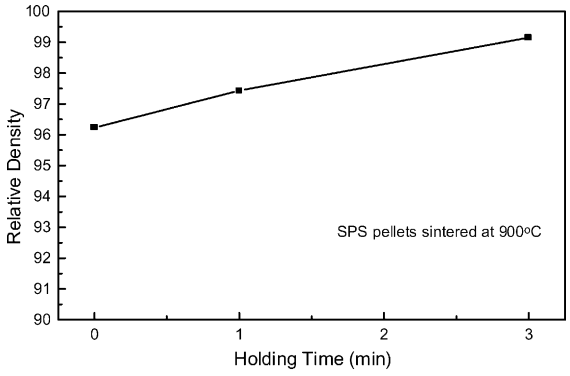


Fig. 3. Dependence of density on holding time for SPS pellets sintered at 900 °C. As for the 0 min sample, the holding time is an estimate near 900 °C.

Fig. 5 shows the X-ray diffraction patterns for SPS pellets sintered at 900 °C following anneal treatment and CIP pellets sintered at 1250 °C for 2 h starting from the same powders. The CIP pellets displayed XRD profiles with the formation of tetragonal phase, while SPS pellets are analyzed as being composed of tetragonal and a small amount of cubic phases. This can be found from peaks (002) and (200), (102) and (201), especially from (001) and (100), (112) and (211) by monitoring of full width half maximum with a step of 0.005° and scanning speed of 0.5°/min. On the contrary, CIP pellets showed clear splitting of tetragonal peaks on these crystal faces. This same result has also been reported by Fang [1] and Takeuchi et al. [6,17], but is different from that of Randall et al. [3] who regarded that the size effect is not evident until sizes approach 40 nm.

It appears that the grain size is strongly related to the paraelectric and ferroelectric transformation. When the grain size is below a certain level the crystallographic cell becomes more and more cubic, just as the increase of temperature affects the phase transition. Shaikh [18] and coworkers have proposed a model that $BaTiO_3$ ceramics consist of cubic grain boundaries and tetragonal interior

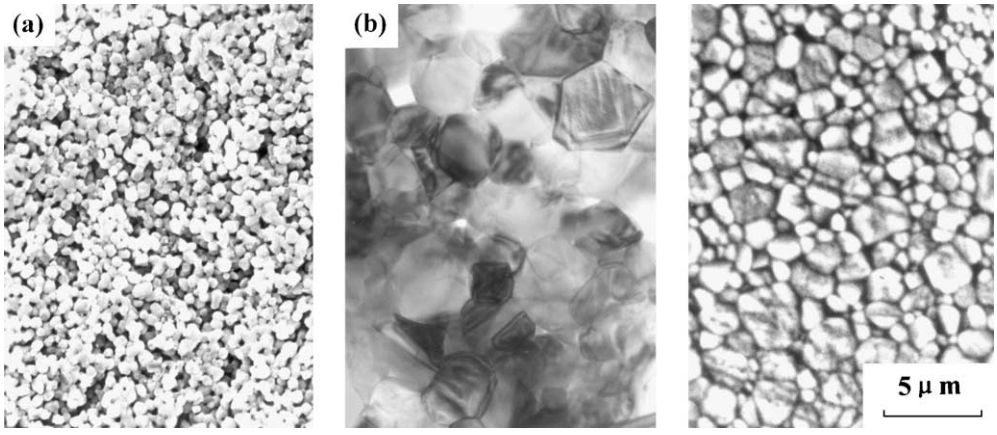


Fig. 4. (a) SEM image and (b) TEM micrograph of $BaTiO_3$ ceramics sintered at 900 °C without hold time by SPS method; (c) SEM micrograph of CIP pellet sintered at 1250 °C for 2 h.

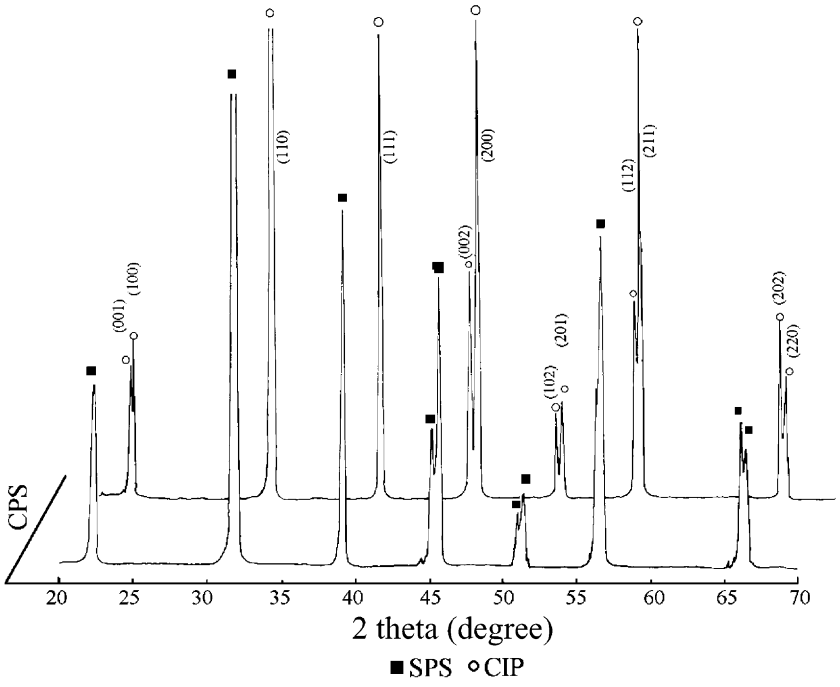


Fig. 5. X-ray diffraction patterns for SPS pellets sintered at 900 °C for 3 min at 50 MPa pressure and CIP pellets sintered at 1250 °C for 1 h in air with the same starting powder as SPS method.

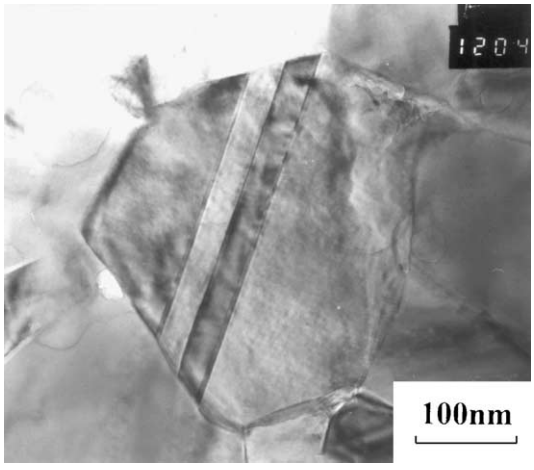


Fig. 6. TEM micrograph illustrating domain structure in $BaTiO_3$ grain.

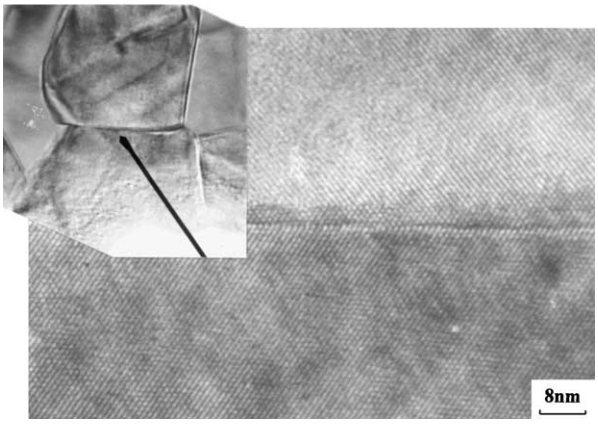


Fig.7. HRTEM micrograph illustrating the boundary region between adjacent grains of $BaTiO_3$ SPS pellets.

grains. Here, the fraction of paraelectric cubic phase increases as the grain size decrease. In our experiment, it is interesting to note that the SPS pellets consisted of mainly 200 nm grains, resulting in a relative small amount of cubic phase compared with that of the CIP pellets.

3.3. HRTEM analysis

HRTEM analysis on SPS pellets sintered at 900 °C without a hold time was carried out. As displayed in Fig. 6, some 180° domains can be clearly seen in the micrographs. No ferroelectric 90° domain structure was observed, which indicates that the specimen is of single domain phase. This is only observed in fine-grained ceramics having a grain size smaller than 1 μm. The same results have been obtained by other researchers [19,20]. The average domain width of domain was calculated to be 30 nm. Some clear twins with obtuse angles were found in the ceramic, which were considered absent in sub-micrometer $BaTiO_3$ ceramic [21]. When the relationship of grain size and grain boundary is studied, a thin boundary width of only 8 Å is observed (Fig. 7). The boundary width is approximately twice the lattice constant of $BaTiO_3$ crystal. It is commonly regarded that for highly densified ceramics with fine

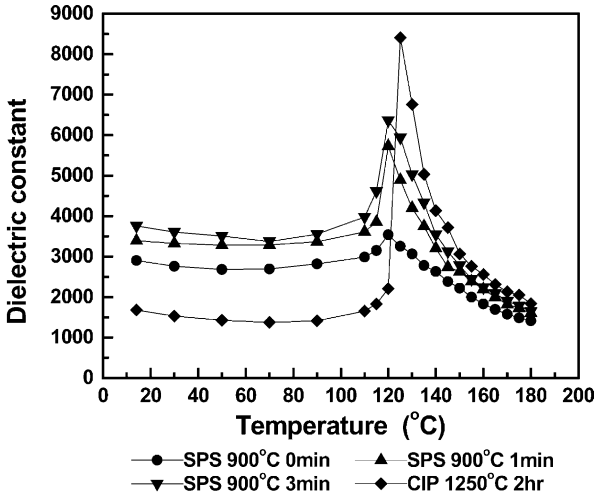


Fig. 8. Dependence of dielectric constant on sintering temperature at a frequency of 1 kHz.

grain size, grain boundary width is nearly twice the lattice constant.

3.4. Dielectric properties

Due to practical difficulties in preparing dense $BaTiO_3$ ceramics with a grain size less than 0.5 μm, few data have been reported for dielectric constant below that grain size. Based on the effective sintering method of SPS, we achieved fine-grained $BaTiO_3$ ceramics with high density. Fig. 8 gives the temperature-dependence for SPS pellets sintered at 900 °C for various hold times. As a comparison, dielectric measurements on CIP pellets sintered at 1250 °C for 2 h are also shown. It is found that all SPS pellets show a dielectric peak at 120 °C, while the peak of CIP happens at a higher temperature of 124 °C. Further, the finest sample of SPS pellets fabricated without hold time displays a flat curve, which indicates a diffuse phase transition (DPT). Meanwhile, SPS pellets of 1 and 3 min hold time with larger grain size showed relatively sharp dielectric peaks, but still show some DPT behavior compared with the micrometer grain-sized ceramics of CIP. Moreover, among the three SPS pellets sintered at 900 °C with different hold times, the finest SPS aero-min pellet displayed the lowest dielectric constant at room temperature. The specimen that has longer hold time displays larger grain size and higher density. High density reduces the effect of pores on weakening dielectric constant. On the other hand, the transforming fraction increases with the decrease of grain size. Also, higher cubic content leads to incomplete development of the tetragonal structure and greater dielectric DPT.

It is noteworthy that the dielectric constant of SPS 0 min is 2900 at room temperature, which is higher than that predicted by other researchers [18,22]. Based on the structure analysis of XRD, i.e., observation of domains and twins, we found that the increase of dielectric constant of fine-grained ceramics is possibly caused by the 180° domain structure. The tetragonal distortion of the perovskite unit cell below the Curie point can no longer be compensated by formation of 90° domains. On the other hand, the presence of twins increased the internal stress beyond the effect of phase transformation, and finally resulted in the increase of dielectric constant. Accordingly, it is not the intention of this paper to set aside the earlier theories suggesting a stress-induced and domain size increase of the dielectric constant in fine-grained $BaTiO_3$. The variation in dielectric properties is possibly caused by a summation of stress effects, domain, and phase structure. This explanation is based on the successful obtaining of fine-grained $BaTiO_3$ ceramics.

4. Conclusions

Dense $BaTiO_3$ pellets with fine grain size were obtained by employing spark plasma sintering at a much lower sintering temperature (900 °C) and shorter sintering time (a few minutes) compared with conditional sintering methods. Under the observation of HRTEM, 180° domains and some twins are observed. The grain boundary width is only 8 Å in the 200 nm grain size ceramics, which is about twice the lattice constant. XRD analysis indicated that the fine-grained ceramics show a small amount of cubic phase, while CIP pellets are of single tetragonal phase. Dielectric measurements show a dependence of dielectric constant on grain size and Diffuse Phase Transition (DPT) phenomenon on fine-grained SPS ceramics. An explanation has been proposed for the unusually high dielectric constant of fine-grained $BaTiO_3$ ceramics.

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