

Grain size effects on piezoelectric properties of BaTiO₃ ceramics prepared by spark plasma sintering

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Abstract Grain size effects on permittivity, piezoelectric constant d_{33} and electric field-induced strain of BaTiO₃ ceramics prepared by spark plasma sintering were studied systematically in this study. It was found that in our studied grain size range they all showed clear grain size effects, while their variations with grain size were distinctly different. With increasing grain size, the permittivity decreases monotonically due to decreased domain wall density, the piezoelectric constant d_{33} keeps increasing because of the increased domain alignment which is related to the increase of 180° domain and decreased clamping effect on 90° domain switching by grain boundaries, the electric field-induced strain maximize at intermediate grain size which is due to the maximization of reversible 90° domain switching.

1 Introduction

Piezoelectric ceramics are important functional materials that can realize the conversion between electrical and mechanical energy. The currently used piezoelectric ceramics are almost lead-based Pb(Zr, Ti)O₃ (PZT) ones due to their excellent piezoelectric properties and good temperature stability. However, lead-free piezoelectric ceramics have attracted more and more attention during

recent years because of the toxicity of lead [1, 2]. In order to achieve higher piezoelectric properties in lead-free piezoelectric ceramics, several attempts have been made, including constructing morphology phase boundaries, which are considered as the origin of high piezoelectric properties in PZT, (K, Na)NbO₃ and BaTiO₃-based ceramics [3–5].

Another important strategy to increase the piezoelectricity of ferroelectric ceramics is the grain size effect [6–8]. Grain size effect is generally referred to the phenomenon that permittivity of ferroelectric ceramics changes dramatically with their grain size and maximizes at a certain grain size. The most studied is the grain size effect on permittivity of BaTiO₃ ceramics. The permittivity maximized around the grain size of 1 μm and it was suggested that the variation of domain wall movement with grain size was the main mechanism for the grain size effect on permittivity [9–11]. It was gradually realized that the piezoelectric properties of ferroelectric ceramics also showed clear grain size effects. The studies of grain size effect on piezoelectric properties are mainly focused on PZT and BaTiO₃ ceramics [12]. However, unlike the grain size effect on permittivity, the grain size effect on d_{33} of ferroelectric ceramics shows diverse trends in ceramics prepared by different techniques and it is quite sensitive to the ceramic processing. Recently it was demonstrated that the grain size effect on d_{33} was easily influenced by the defects such as vacancies in ceramics which are usually produced at high sintering temperature [9, 13]. These defects can have a strong domain wall pinning effect and thus the piezoelectric properties are influenced. Furthermore, the porosity of ceramics also has a big influence on the grain size effect on piezoelectricity.

In order to minimize the influence of defects as well as porosity and have a clear picture on the grain size

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dependences of piezoelectric properties in ferroelectric ceramics, spark plasma sintering and fine BaTiO₃ powders were used in this study. Three types of BaTiO₃ ceramics with different grain size were fabricated and the grain size effects on d_{33} and electric field-induced strain were studied.

2 Experimental

Fine BaTiO₃ powders with the particle size of 50 nm (Fig. 1) were used in this study. Dense BaTiO₃ ceramics with different grain sizes were sintered using spark plasma sintering (SPS, HPD-25/1 FCT systeme GmbH) at different temperatures (1000, 1040, and 1080 °C) under a uniaxial pressure of 85 MPa for 5 min. The sintered samples were further annealed at 900 °C for 2 h. The density of ceramics was measured by the Archimedes method. The microstructure of BaTiO₃ ceramics was observed using a scanning electron microscope (SEM; JEOLJSM 6300). For electrical characterization, ceramic specimens were coated with silver paint on the top and bottom surfaces and fired at 600 °C for 20 min. The dielectric properties were measured using an impedance analyzer (Agilent 4294A). The ferroelectric polarization hysteresis loops (P–E loops) and electric field-strain loops (S–E loops) were measured using a ferroelectric measurement tester at room temperature. Poling was accomplished at 105 °C in silicon oil under 3.0 kV/mm for 30 min. The d_{33} value was measured using a Berlincourt-type d_{33} meter (YE 2730A).

3 Results and discussion

Sintering temperature is a key factor that affects the grain size, and consequently BaTiO₃ ceramics have been sintered at different temperatures. The fractured surface of BaTiO₃ ceramics were displayed in Fig. 2. The ceramic sintered at

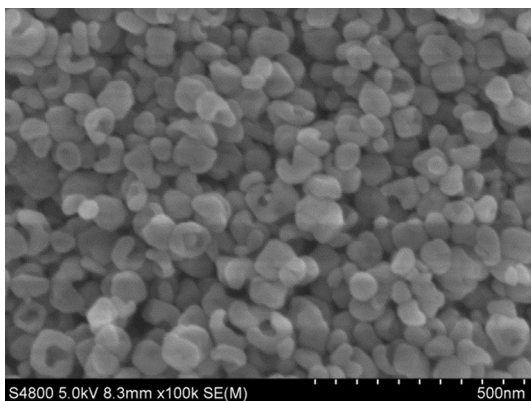


Fig. 1 SEM picture of fine BaTiO₃ powders with the particle size of 50 nm

1000 °C shows a uniform grain size distribution with an average grain size of about 0.7 μm (Fig. 2a). With increasing sintering temperature the average grain size increases gradually to 8 μm when sintered at 1080 °C (Fig. 2c). Particularly, as shown in Fig. 2, all ceramics show quite dense microstructures, which can efficiently exclude the influence of porosity.

Table 1 summarizes the dielectric and piezoelectric properties of BaTiO₃ ceramics with different grain sizes. The permittivity of BaTiO₃ ceramic with an average grain size of 0.7 μm shows a high permittivity of 4300, with increasing grain size the permittivity decreases dramatically and the ceramic with an average grain size of 8 μm shows a permittivity of only 2200. This grain size dependence of permittivity is consistent with most of the reports for BaTiO₃ ceramics. It was suggested that the increased domain wall mobility due to increased domain wall density with decreasing grain size is responsible for this observed grain size dependence [6, 9–11, 13–15]. Further, the dielectric loss of these BaTiO₃ ceramics is considerably small due to the relatively lower sintering temperatures. However, the grain size dependence of d_{33} is opposite to the grain size dependence of permittivity. With increasing the average grain size, the d_{33} of BaTiO₃ ceramics increases monotonically from 100 pC/N at 0.7 μm to 280 pC/N at 8 μm. This result is also different from many grain size effect studies in BaTiO₃ ceramics previously reported [8, 16]. According to this result, the underlying mechanism for grain size effect on d_{33} should be different from that on permittivity. The high domain wall density which is responsible for high permittivity should not be the origin of high d_{33} in BaTiO₃ ceramics, at least in our studied grain size range.

As we all know, a piezoelectric ceramic needs to be poled to show piezoelectricity. During poling process the domains aligned gradually from a randomly orientated state. After removal of electric field a small portion of domains will stay in poled state although the major portion of domains switches back to their original states. The domain alignment degree after poling is quite important for high d_{33} and thus this maybe the origin for different grain size influence on permittivity and d_{33} . In order to compare the domain alignment after poling for BaTiO₃ ceramics with different grain sizes, the polarization-electric field (P–E) and current-electric field (I–E) hysteresis loops were measured at room temperature and the results are shown in Fig. 3. All BaTiO₃ ceramics exhibit large saturated polarization around 25 μC/cm², which can be mainly attributed to the formation of micron-sized grains possessing nano-scale mosaicity as suggested by previous report [17]. With increasing grain size, the P–E loops of BaTiO₃ ceramics becomes more saturated with larger remnant polarization and smaller coercive field determined from the current

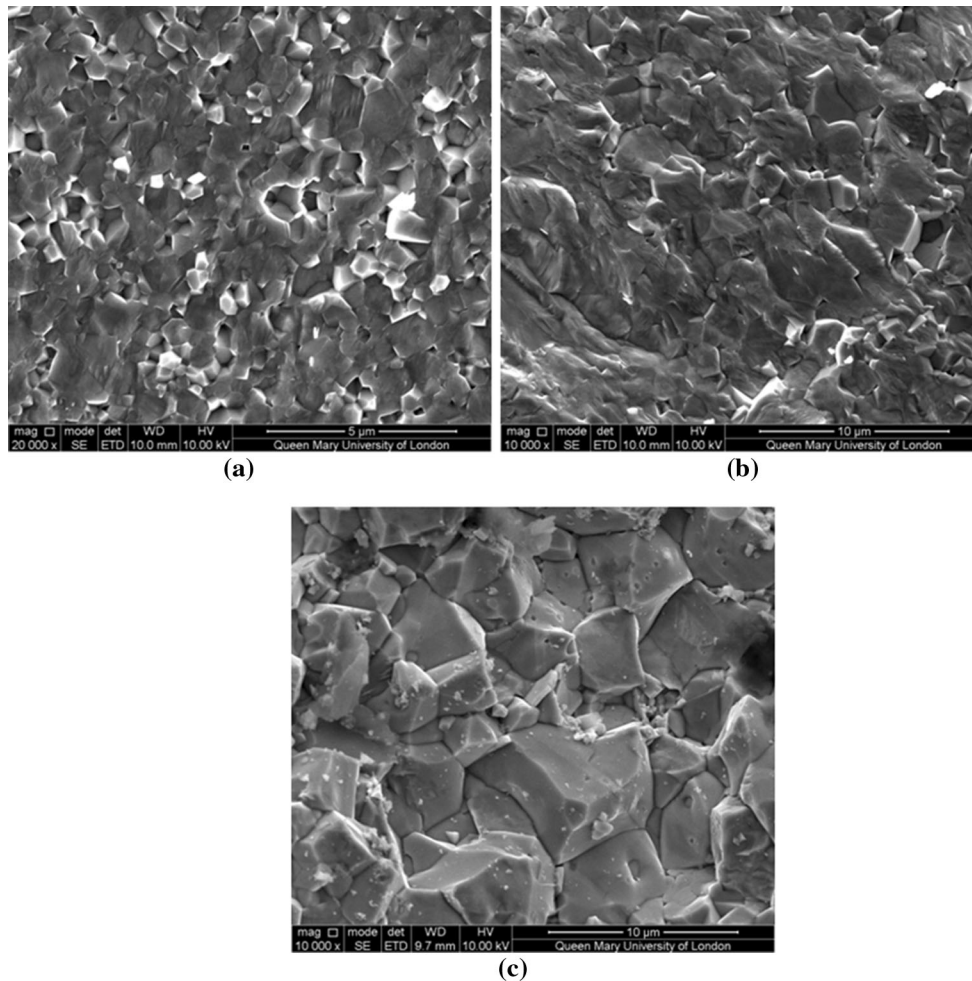


Fig. 2 SEM pictures of the fractured surface of BaTiO₃ ceramics sintered at different temperatures. **a** 1000 °C, **b** 1040 °C, and **c** 1080 °C

Table 1 Summarizes the dielectric and piezoelectric properties of BaTiO₃ ceramics with different grain sizes

| Average grain size (μm) | 0.7 ± 0.22 | 1.8 ± 0.36 | 8 ± 1.27 |
|-------------------------------|------------|------------|----------|
| Temperature (°C) | 1000 | 1040 | 1080 |
| Permittivity | 4300 | 3600 | 2200 |
| tanδ (%) | 0.8 | 1.0 | 1.1 |
| <i>d</i> ₃₃ (pC/N) | 100 | 210 | 290 |

peak in the I–E loops [18]. The BaTiO₃ ceramic with an average grain size of 0.7 μm shows a slim P–E hysteresis loop with a small remnant polarization of 5.6 μC/cm². When the grain size is increased to 8.0 μm the BaTiO₃ ceramic shows a saturated P–E loop with a much larger remnant polarization of 14.7 μC/cm². The increase of remnant polarization with increasing grain size can be interpreted as a result of the decreased clamping effect from grain boundaries. With increasing grain size, the grain boundary areas decrease correspondingly. In fine grained

BaTiO₃ ceramics, the grain boundaries can exert a strong restoring force on domain reorientations, especially on 90° domain reorientations which will cause internal stress, with the removal of electric field. Therefore most of the 90° domain reorientations upon electric field will switch back and gives rise to the small remnant polarization. The decreased grain boundary clamping effect increases the remnant polarization with increasing grain size.

It can be observed that the grain size dependence on remnant polarization shows good consistency with the grain size dependence on *d*₃₃ in BaTiO₃ ceramics. Thus it can be concluded that higher domain alignment degree after poling is essential for higher *d*₃₃ in BaTiO₃ ceramics in our studied grain size range.

Figure 4 shows the bipolar (Fig. 4a) and unipolar (Fig. 4b) electric field-induced strain behaviours of as prepared and poled BaTiO₃ ceramics with different grain sizes respectively. From Fig. 4a it can be seen that all BaTiO₃ ceramics show symmetrical butterfly-shape strain-electric field (S–E) hysteresis loops [19]. With increasing

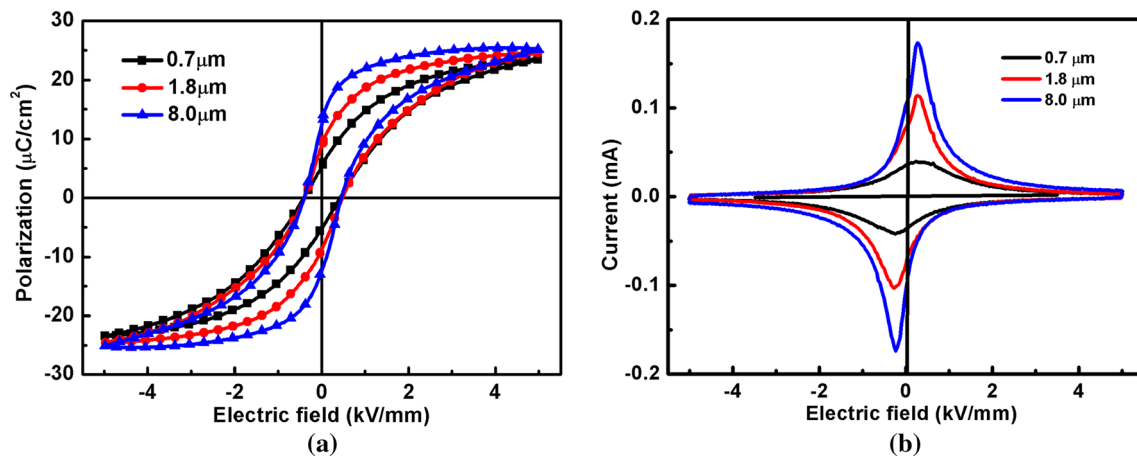


Fig. 3 The polarization-electric field (P-E) hysteresis loops (a) and current-electric field (I-E) hysteresis loops (b) of BaTiO₃ ceramics with different grain sizes

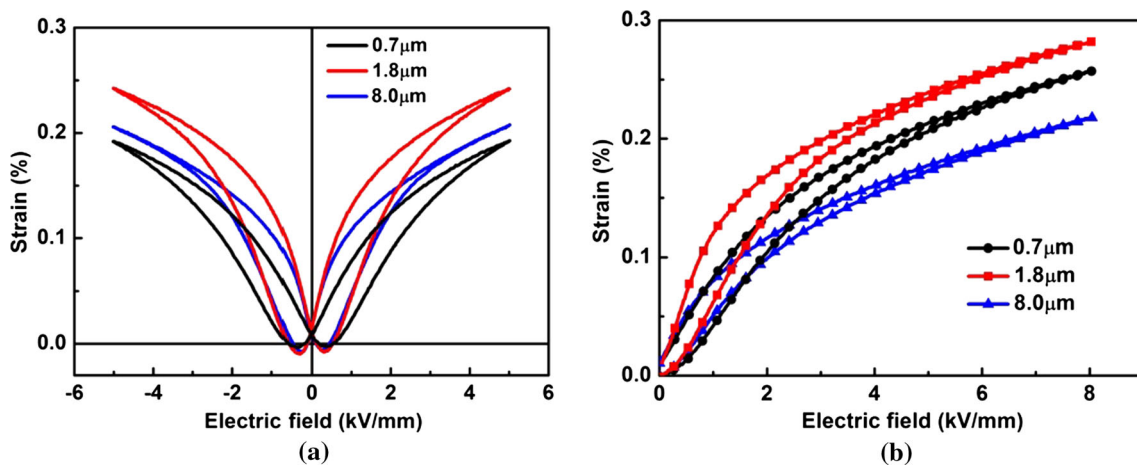


Fig. 4 The bipolar (a) and unipolar (b) electric field-induced strain behaviours of as prepared and poled BaTiO₃ ceramics with different grain sizes respectively

grain size, the maximum strain that can be achieved at 5 kV/mm firstly increased and then decreased with a peak value of 0.25 % for ceramic with an average grain size of 1.8 μm . After poling process the unipolar strain of ceramics with different grain sizes was measured and the results are shown in Fig. 4b. The samples can stand an electric field as large as 8 kV/mm suggesting that all samples have a good crystal structure with little defects due to the lower sintering temperature. All the samples show slim unipolar S–E loops with small remnant strain which are consistent with previous reports. The BaTiO₃ ceramic with an average grain size of 0.7 μm shows a large strain of 0.257 % at 8 kV/mm. With increasing the grain size the maximum strain increases to 0.282 % which is a relatively large strain in BaTiO₃ ceramics. With further increasing the grain size, the maximum strain that can be achieved decreases dramatically to 0.217 % for BaTiO₃ ceramics

with an average grain size of 8.0 μm . The grain size dependences on bipolar and unipolar electric field-induced strain show similar trends. However, the grain size dependence on electric field-induced strain is different from the grain size dependences on both permittivity and d_{33} . It means that high electric field-induced strain in BaTiO₃ ceramics has a different underlying mechanism which was suggested by previous report [20]. There are two factors determining the strain value in piezoelectric ceramics: the maximum achievable strain during the very first electric field cycle and the remnant strain after the removal of electric field. The difference between the two values is the effective strain that can be used in actuators [21–23]. For fine grained sample, the maximum achievable strain during the very first electric field cycle is small due to the limited 90° domain switching determined by the larger clamping effect from grain boundaries. Larger

grained sample usually have more amounts of 90° domain switching due to less clamping effect from grain boundaries, and therefore larger achievable strain [20]. However, the remnant strain after the removal of electric field is also larger due to less clamping effect from grain boundaries. Consequently, the effective strain is also relatively smaller. Only when the maximum achievable strain and remnant strain are well balanced in intermediate grained sample, a larger strain can be achieved.

4 Conclusions

The grain size influence on permittivity, d_{33} and electric field-induced strain of BaTiO₃ ceramics prepared by SPS were found to be totally different from each other in the grain size range of 0.7–8.0 μm. Due to the lower sintering temperature and high density for BaTiO₃ ceramics in this study, the studied grain size dependences were thought to be not influenced by other external factors such as defects and porosity. In this case, with increasing grain size, the permittivity decreases, the d_{33} increases and the strain first increases and then decreases. The domain wall density is essential for permittivity, the domain alignment degree is important for d_{33} and the reversible domain switching is favourable for electric field-induced strain.

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