Field-assisted sintering of undoped BaTiO3: microstructure evolution and dielectric permittivity

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Field-assisted sintering of undoped BaTiO₃: Microstructure evolution and dielectric permittivity

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Abstract

We report, for first time, how electric fields influence the sintering of undoped BaTiO₃, a ferroelectric material, and how this process affects the microstructure and the dielectric properties. Flash sintering is achieved at a furnace temperature of 688 °C under a field of 500 V cm⁻¹, producing specimens that are 94% dense. As a consequence, the grain size is much finer than in conventional sintering, which is shown to influence the Curie temperature and dielectric permittivity. Data obtained at different strengths of the electrical field, and current limits imposed on the specimen are presented in the form of a “processing map” that separates the safe region, where sintering is uniform, from the fail region, where the current flow in the sample becomes localized. The map illustrates that ceramics can respond by different mechanisms, with the dominant mechanism changing with the strength of the electrical parameters.

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Keywords: BaTiO₃; Flash sintering; Microstructure; Permittivity

1. Introduction

Barium titanate (BaTiO₃), a ferroelectric material with perovskite structure, is used in high-permittivity capacitors, transducers, ferroelectric memories and positive temperature coefficient (PTC) resistors.¹,² Conventional sintering of barium titanate usually requires temperatures ≥1250–1300 °C.²,⁴ Liquid phase that may form during sintering can however lead to accentuated abnormal grain growth.³,⁵

Hot-isostatic-pressing and spark plasma sintering are expected to produce microstructures with smaller grain sizes.⁴,⁶–⁹ In this article we report the results from field-assisted sintering where the electrical field is applied directly to an otherwise freely sintering specimen placed in a conventional furnace. This process, also known as flash sintering, has been shown to enhance the sintering kinetics of several materials.¹⁰–¹⁶ We find that this process leads to dense, fine-grained and high-permittivity ceramics of barium titanate. The furnace temperatures and process times are considerably below conventional sintering.

2. Experimental procedure

BaTiO₃ was synthesized by a hydrolysis method using Ba(OH)₂ and Ti alkoxide, and calcined at 700 °C for 2 h, resulting in a high-purity (>99.98%) powder with estimated specific surface area of 16 m²/g, average particle size of 70 nm (within a narrow distribution of ±8 nm) and a Ba/Ti ratio of 1.002. For sample preparation, the powders were cold-pressed at uniaxial pressure of 280–300 MPa in a dogbone-shaped die, giving green bodies with a gage section length of 20 mm, a rectangular cross section of 3.5 mm × 1.6–2.0 mm, and green density ranging here from 60 to 64% of theoretical density (TD = 6.02 g/cm³). A

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Sintering was carried out in a molybdenum di-silicate furnace, in ambient air. Shrinkage was measured with a CCD camera that recorded photographs of the specimen at approximately 1 s intervals. The linear sintering strain was calculated from \( \varepsilon = \ln(L/L_0) \), where \( L \) is the time dependent length of the gauge section, and \( L_0 \) its initial value. Assuming shrinkage to be isotropic, the relative density of the specimens was then obtained from the expression \( \ln(\rho/\rho_0) = 3 \varepsilon \), where \( \rho_0 \) is the green density at the start of the sintering experiment and \( \rho \) is the density during the sintering process.

Electric field-assisted sintering experiments were carried out by following the procedure described in Ref. 14. The specimen was suspended into the furnace with platinum wires which also served as the field and current carrying electrodes. The furnace temperature was raised with a constant heating rate of 10 °C min \(^{-1} \), and the voltage was applied to the specimen when the furnace reached 500 °C. The current flowing through the specimen increased abruptly at the onset of the flash, at which point the power supply was switched (from voltage) to current control; this led to a fall in the voltage as the conductivity of the specimen continued to increase, as discussed in earlier papers, see e.g., Ref. 15. The experiments were usually ended a few minutes after the onset of the flash. In all these experiments (with a couple of exceptions described later) the current was set to a limit of 60 mA, which corresponds here to a current density of about 9.3 mA mm \(^{-2} \).

To get further information on conductivity behavior during sintering, experiments were also carried out at isothermal furnace temperature. The specimens were heated up to a given temperature in the 650–1100 °C range, followed by a step-wise application of the electric field. A wide range of fields and current density limits were tested. The experiments were ended less than 1 min after the onset of the flash phenomenon.

Conventional sintering experiments were carried out at a constant heating rate (also 10 °C min \(^{-1} \)), without the application of an electric field (called the 0 V experiment). In this instance, the specimen had to be heated to 1300 °C to achieve a minimum density of 97%. For microstructure comparison with field-assisted sintering, conventional sintering at 1300 and 1350 °C was also considered.

The grain size of the specimens was measured over an area of about 3.0 mm \( \times \) 1.5 mm. The sample was polished down to a finish of 1 μm, followed by thermal etching at 1100 °C for 30 min in ambient air. The specimens were sputter coated with 2.5 nm of Au–Pd, and imaged in a field-emission scanning electron microscope (JEOL JSM-7401F). The micrographs were digitally analyzed and values of average grain size were estimated using the linear intercept method, as described elsewhere, in accordance with ASTM standards. To assess the possibility of grain growth during thermal etching, as-sintered samples were also fractured and the grain size estimated from SEM images of the fracture surfaces, and then compared with the values from the polished and etched cross-sections.

For electrical measurements, the specimens were cut into rectangular blocks and finished with a surface grinder using a 300 grit diamond wheel, resulting in samples with area of 9.7–12.3 mm\(^2\), and thickness of 1.0–1.5 mm. Platinum electrodes were painted onto both major surfaces, followed by drying at 550 °C for about 10 min. An impedance analyzer (HP 4192A) was used for obtaining permittivity data from room temperature to about 310 °C at 100 kHz.

### 3. Results and discussion

Fig. 1 shows the behavior of strain for the conventional and several electric field-assisted sintering experiments. The results are typical of flash sintering behavior where the electric field reduces considerably the (furnace) sintering temperature. The power dissipation and physical density from a few experiments are depicted in Fig. 2. Note the peak in power dissipation followed by a decline in its magnitude, which is a characteristic of this phenomenon. There is however a subtle difference between the results at 150 V cm\(^{-1}\), where the onset of the flash regime occurs after the sample has sintered to a considerable degree, and those above 250 V cm\(^{-1}\), where the onset of flash coincides with sintering.

Such behavior has been reported before, and reflects two different mechanisms of field-assisted sintering. The gradual
show that high-density BaTiO$_3$ electroceramics can be made at $\sim 1300 \degree$C.

Sintering conditions, density ($\rho$, in percentage of theoretical density (TD), and flash sintering temperature ($T_{\text{FLASH}}$), where applying, of BaTiO$_3$ specimens conventionally and flash sintered.

<table>
<thead>
<tr>
<th>Sintering conditions</th>
<th>$\rho$ (% TD)</th>
<th>$T_{\text{FLASH}}$ ($\degree$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1350 $\degree$C/1 h$^a$</td>
<td>98.4</td>
<td>n/a</td>
</tr>
<tr>
<td>1300 $\degree$C/5 min$^a$</td>
<td>97.2</td>
<td>n/a</td>
</tr>
<tr>
<td>150 V cm$^{-1}$/60 mA/15 min</td>
<td>97.1</td>
<td>900</td>
</tr>
<tr>
<td>200 V cm$^{-1}$/60 mA/3 min</td>
<td>94.3</td>
<td>825</td>
</tr>
<tr>
<td>250 V cm$^{-1}$/60 mA/3 min</td>
<td>94.4</td>
<td>822</td>
</tr>
<tr>
<td>300 V cm$^{-1}$/60 mA/3 min</td>
<td>95.6</td>
<td>760</td>
</tr>
<tr>
<td>375 V cm$^{-1}$/60 mA/2 min</td>
<td>95.3</td>
<td>748</td>
</tr>
<tr>
<td>425 V cm$^{-1}$/60 mA/2 min</td>
<td>94.5</td>
<td>719</td>
</tr>
<tr>
<td>500 V cm$^{-1}$/60 mA/1 min</td>
<td>94.2</td>
<td>688</td>
</tr>
<tr>
<td>1000 V cm$^{-1}$/60 mA/1 min</td>
<td>91.6</td>
<td>612</td>
</tr>
</tbody>
</table>

$^a$ Conventional sintering.

$^b$ Furnace temperature.

enhancement in sintering has been called FAST or Type A sintering, and the nearly stepwise sintering as flash or Type B behavior. The first has been explained in terms of reduced rate of grain growth under electric field. The underlying mechanism for flash sintering remains so far unclear. Both Joule heating and electric field-induced generation of defects have been proposed as the underlying mechanism for flash sintering. We shall comment further on this issue later in this article.

The experimental parameters and the results from the present experiments, shown in Fig. 1, are summarized in Table 1. They show that high-density BaTiO$_3$ electroceramics can be made in this way at furnace temperatures that are $\geq 500 \degree$C, or more, below the temperature required in conventional sintering. This is certainly a consequence of enhanced charge and mass transport processes under electric field action.

The conductivity data of various specimens calculated from the instantaneous values of the current, with the power supply set under voltage control, are shown in an Arrhenius plot in Fig. 3. The gradual increase in conductivity for $E \geq 375$ V cm$^{-1}$ results from a transition to flash sintering. The case of 250 V cm$^{-1}$ represents the change from nominal to flash behavior. The dotted line shows the Arrhenius fit to the nominal data for conductivity, by considering a simple expression of type: $\sigma = \sigma_0 \exp (-\Delta H/kT)$, in which $\sigma_0$ is the pre-exponential factor, $\Delta H$ the activation energy, $k$ the Boltzmann’s constant, while $T$ stands for the absolute temperature. In the linear regime, shown by the Arrhenius fit, the furnace and sample temperatures coincide.

The microstructure of the specimen conventionally sintered at $1300 \degree$C is contrasted in Fig. 4 to the specimen sintered under an electric field of 250 V cm$^{-1}$. The former shows a bimodal-like microstructure with larger grains. The average grain size ($D$) is approximately 5.2 $\mu$m. This trend to accentuated abnormal grain growth is well known in BaTiO$_3$-based ceramics, and arises from development of a liquid phase-assisted sintering mechanism (via eutectic reaction at $\sim 1320 \degree$C) for specimens heat treated at temperatures approaching or greater than $1300 \degree$C. The much finer grain size in the flash sintered specimens suggests the absence of the liquid phase and, therefore, a specimen temperature of less than $1300 \degree$C.

The values of the grain size, $D$, for various specimens are listed in Table 2. The grain size measured from polished cross-sections, which were thermally etched, and from the fracture surfaces of as-sintered samples were identical, except for the 500 V cm$^{-1}$ case where the thermally etched samples gave a slightly larger grain size. This is presumably because the very

<table>
<thead>
<tr>
<th>Sintering conditions</th>
<th>$D$ ($\mu$m)</th>
<th>$\varepsilon'(35 \degree$C) ($\times 10^3$)</th>
<th>$\tan\delta(35 \degree$C) ($\times 10^{-2}$)</th>
<th>$T_C$ ($\degree$C)</th>
<th>$\varepsilon'_m$ ($\times 10^3$)</th>
<th>$\tan\delta_m$ ($\times 10^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1350 $\degree$C/1 h$^a$</td>
<td>15.0</td>
<td>1.93</td>
<td>3.2</td>
<td>132</td>
<td>9.05</td>
<td>5.8</td>
</tr>
<tr>
<td>1300 $\degree$C/5 min$^a$</td>
<td>5.2</td>
<td>2.29</td>
<td>3.3</td>
<td>132</td>
<td>10.16</td>
<td>6.6</td>
</tr>
<tr>
<td>150 V cm$^{-1}$/60 mA/15 min</td>
<td>1.1</td>
<td>3.54</td>
<td>2.7</td>
<td>127</td>
<td>6.05</td>
<td>2.2</td>
</tr>
<tr>
<td>250 V cm$^{-1}$/60 mA/3 min</td>
<td>0.6</td>
<td>3.32</td>
<td>3.0</td>
<td>128</td>
<td>5.99</td>
<td>2.8</td>
</tr>
<tr>
<td>375 V cm$^{-1}$/60 mA/2 min</td>
<td>0.4</td>
<td>2.62</td>
<td>3.9</td>
<td>129</td>
<td>5.33</td>
<td>4.1</td>
</tr>
<tr>
<td>500 V cm$^{-1}$/60 mA/1 min</td>
<td>0.3–0.4$^a$</td>
<td>2.15</td>
<td>2.6</td>
<td>128</td>
<td>3.62</td>
<td>2.4</td>
</tr>
</tbody>
</table>

$^a$ Occurrence of abnormal grain growth (conventional sintering).

$^b$ In this instance the fracture surface yielded a smaller grain size than the polished and thermally etched sample.
The small grain size of this sample led to some grain growth during thermal etching. Note that the grain size of 300 nm given in Table 2 is only about 4.3 times the starting mean particle size (70 nm).

The values for the grain size measured in these flash sintering experiments are comparable to those obtained in hot-isostatic-pressing and spark plasma sintering experiments 4,6-9.

The uniformity of microstructure and densification in flash sintering is influenced by the current limit. In the present work we find that there is a transition from uniform to non-uniform sintering as the current limit is increased beyond a certain point.

The micrographs shown in Fig. 5 are a representative example of microstructure appearance after occurrence of this transition from “safe” to “fail” conditions, when the current limit was in this case increased from 15.4 mA mm$^{-2}$ to 77.2 mA mm$^{-2}$, at an applied field of 150 V cm$^{-1}$. At the higher limit, the current through the specimen became localized, creating a tunneling-like physical damage (with melting trace) in the direction of the electric field. The grain size is highest within the localized region, where it is 85 μm in Fig. 5a.1. At the edge of the localized region it is 22 μm as shown in Fig. 5a.2, and reduces to the nominal value of 1.4 μm at a distance from the hole as given.
in Fig. 5a.3. We suggest that grain coarsening within and near the hole should have been the result of liquid phase-assisted sintering due to a significant increase in the local temperature (most likely well above 1350–1400 °C). In contrast, at a distance from the hole, where a dense microstructure with grain sizes close to 1 μm is observed, it may be said that the temperature stayed significantly below the eutectic point (i.e., T < 1320 °C). The same information may also be inferred for those samples discussed in Table 2 and showing average grain sizes < 1 μm.

These observations are consistent with the idea that flash sintering is related not only to Joule heating but also to defect generation. In a recent study on flash processed yttria-doped zirconia, the finding of a residual defect density has also been attributed to the defect mechanism.

The localization of current flow represents a transition in mechanism from uniform sintering to highly non-uniform microstructure which we called above as the “safe” and “fail” conditions. This idea is developed into a processing map shown in Fig. 6. The map is drawn with the current density and the electric field as the axes. These data were obtained from isothermal furnace temperatures. The temperatures are marked within parenthesis; they range from 650 to 1100 °C. The right-hand scale of Fig. 7 shows the loss tangent at 35 °C for the Curie temperatures (Tc) listed in Table 2. Tc decreases from 312 °C for conventionally sintered samples to 128 ± 1 °C for flash sintered specimens.

The above trends are well known for BaTiO3-based ceramics and arise from (i) a progressive change from tetragonal to pseudo-cubic structure (volume effect-related gradual loss of ferroelectricity) and (ii) the increase in grain-boundary density (low-permittivity phase-related surface effect) with decreasing grain size. The inset in Fig. 7 shows the effect of grain size on the permittivity at 35 °C. The effect separates into two regimes, at first rising and then declining with grain size. The rising side of the curve, when D < 1 μm, is explained by the reasons just given. At larger grain size, where 1 < D < 10 μm, the decline in permittivity is ascribed to a decrease in the mobility of the ferroelectric 90° domain walls, whose width decreases as the square root of D. The right-hand scale of Fig. 7 shows the loss tangent at 100 kHz, as a function of temperature. These data are also included in Table 2. The third column gives the values for the loss tangent at 35 °C, while the sixth column gives its maximum values measured at the Curie temperature. Conventionally and flash sintered samples have comparable values for the loss tangent at 35 °C (revealing less than 5%). However, at the Curie temperature the flash sintered samples show a significantly lower loss, also as a consequence of the bulk- and surface-related grain size effects mentioned above.

4. Conclusions

We have shown that electric field-assisted processing of undoped barium titanate precludes liquid phase-enhanced sintering and abnormal grain growth that is often prevalent in conventional sintering. Nearly fully dense specimens with grain sizes as low as 300–400 nm can be produced. Higher applied fields lead to smaller grain sizes, while higher settings of the
current limit increase the grain size. Very high current setting leads to a different mechanism of electrical behavior whereby the current becomes localized into a narrow channel through the specimen. These results point toward the importance of recognizing that ceramics can respond by different mechanisms depending on the setting of the electrical parameters in the experiment. One recalls the significance of deformation mechanism maps where the dominant mechanism can change with the applied stress, the temperature and the grain size.

Finally, the ferroelectric properties (Curie temperature and dielectric permittivity) of these materials were found to depend on the grain size, as has been reported in the literature.

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