Research Article

Temperature dependence of dielectric nonlinearity of BaTiO₃ ceramics

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Abstract

In many commercially utilized ferroelectric materials, the motion of domain walls is an important contributor to the functional dielectric and piezoelectric responses. This paper compares the temperature dependence of domain wall motion for BaTiO₃ ceramics with different grain sizes, point defect concentrations, and formulations. The grain boundaries act as significant pinning points for domain wall motion such that fine-grained materials show smaller extrinsic contributions to the properties below the Curie temperature and lower residual ferroelectric contributions immediately above the Curie temperature. Oxygen vacancy point defects make a modest change in the extrinsic contributions of undoped BaTiO₃ ceramics. In formulated BaTiO₃, extrinsic contributions to the dielectric response were suppressed over a wide temperature range. It is believed this is due to a combination of reduced grain size, the existence of a core-shell microstructure, and a reduction in domain wall continuity over the grain boundaries.

Keywords: Ferroelectrics, dielectric nonlinearity, grain size, ceramics

INTRODUCTION

It is well documented that the dielectric and piezoelectric responses of many ferroelectric materials include contributions from the motion of domain walls, even when the electric field used to excite the material is well below the coercive field[1-6]. This motion of domain walls is important to understand, as it will govern much of the field, time, and frequency dependence of the properties of a ferroelectric material. As an

example, domain wall motion contributes substantially to the room temperature permittivity of $BaTiO_3$-based multilayer ceramic capacitors. Similarly, up to 75% of the piezoelectric response of soft $PbZr_{1-x}Ti_xO_3$ ceramics arises from domain wall motion, albeit at the expense of increased hysteresis. The relative extent of domain wall motion for a given material depends explicitly on the history of the sample, the sample microstructure[7,8] and orientation, and the excitation conditions. For example, the following factors are critical to the observed extent of extrinsic contributions to the properties:

Electric field

Higher amplitudes of the AC electric field ($E_{AC\ 0\text{-}pk}$) act to drive domain walls more strongly and can substantially increase the extrinsic contributions to the properties. This increases the relative permittivity and loss tangent with the AC field, which is called dielectric nonlinearity. Often, the increase in relative permittivity is linear with AC electric field, producing the so-called Rayleigh regime (from a modified version of the Rayleigh law originally developed for magnetic materials)[9], i.e.,

$$\varepsilon' = \varepsilon'_{init} + \alpha' E_{AC\ 0-pk}$$

where ε' is the relative permittivity, ε'_{init} is the reversible Rayleigh coefficient that includes both the intrinsic response and reversible motion of domain walls or phase boundaries, and α' is the irreversible Rayleigh coefficient[10]. The Rayleigh law is typically observed up to modest electric fields under conditions where the domain structure is unchanged during the measurement and the distribution of the restoring forces for the domain walls is Gaussian[11]. In cases where the domain wall density is changed by the applied field, the Rayleigh law will not be observed, and a more complex formalism, such as first-order reversal curves, needs to be employed[12-16]. In many but not all ferroelectric materials, significant levels of domain nucleation are observed at $E_{AC\ 0\text{-}pk}$ exceeding ~a third to a half of the coercive field.

In contrast, because DC biases stabilize the domain state, they also act to suppress extrinsic contributions to the properties. This produces a far stronger DC bias dependence of the relative permittivity[4] than would be predicted based on phenomenological descriptions of the field dependence of the intrinsic permittivity (e.g., intrinsic dielectric stiffening)[17,18]. This progressive loss of the extrinsic contributions to the permittivity is problematic in multilayer ceramic capacitors where the voltage saturation significantly depresses the usable capacitance[19]. In contrast, the suppression is very helpful in some piezoelectric sensing applications, as it increases the figure of merit = piezoelectric coefficient/relative permittivity[20].

Temperature

There is a strong coupling between temperature and extrinsic contributions to the properties. First, domain wall motion is thermally activated such that domain walls become more mobile as temperature increases. Therefore, extrinsic contributions typically rise as the Curie temperature is approached. Other ferroelectric-ferroelectric phase transitions also tend to favor the motion of the mobile interfaces and will induce increases in the extrinsic contributions. Secondly, because domain wall and phase boundary motions are inherently dissipative, substantial levels of extrinsic contributions can increase the sample temperature[21]. Thirdly, changes in temperature can perturb the domain structure and so de-age the material, increasing the extrinsic contributions temporarily.

Time

Domain structures, especially in ceramic materials, are rarely fully stable as a function of time. Thus, over the course of time, the domain structure progressively seeks lower energy configurations. As this occurs, the remaining domain walls tend to be less mobile. This is one of the contributions to the aging of the dielectric

or piezoelectric response[22]. Time dependence is also observed in cases where poorly poled piezoelectrics are excited with unipolar waveforms, as is sometimes done in piezoelectric microelectromechanical systems. In this case, the sample poles progressively during use, increasing the remanent piezoelectric coefficient but decreasing the achievable strain during actuation due to progressive loss of the poling strain that is caused by polarization alignment. It is also critical to note that these factors of microstructure, time, temperature, and field are all inextricably linked such that the aging rates will depend on the amplitude of the field used for their characterization[23].

This paper illustrates the temperature dependence of the domain wall contributions to the dielectric properties of $BaTiO_3$ ceramics, with an emphasis on the role of phase transitions, grain size, core-shell microstructures, and point defect concentrations in the response. The resulting temperature dependence of the dielectric response is a complex interplay between these factors.

EXPERIMENTAL PROCEDURE

Samples

Undoped $BaTiO_3$ ceramics were prepared using a $BaTiO_3$ powder (BT02, with a Ba/Ti ratio of 0.996, Sakai Chemical Industry Co., Ltd., Sakai, Japan). To study the effect of grain size, $BaTiO_3$ ceramics with grain sizes of 1.2 μm and 76 μm were prepared. The former was prepared by sintering a $BaTiO_3$ compact at 1,300 °C for 2 h and post-annealing the sintered body at 1,000 °C for 9.5 h[24], while the latter was prepared by sintering the compact at 1,350 °C for 2 h[25]. The grain sizes were measured from the microstructures of polished and chemically etched ceramic surfaces observed by scanning electron microscopy (SEM). Figure 1A and B shows the SEM images of the undoped $BaTiO_3$ ceramics. Two grain lengths were measured for each grain, and the average of these two lengths was calculated for more than 90 grains. The grain size given is the average of the two-length average, and the error bar for the grain size is the standard deviation. The grain sizes were calculated to be 1.2 ± 0.5 μm and 76 ± 37 μm for the $BaTiO_3$ ceramics sintered at 1,300 °C and 1,350 °C, respectively. To study the effect of oxygen partial pressure (pO_2) during sintering, $BaTiO_3$ ceramics were sintered at 10^{-9} atm pO_2 at 1,300 °C for 2 h[24]. A microstructure similar to that of the undoped $BaTiO_3$ ceramics sintered at 1,300 °C in air (10^{-2} atm pO_2) was observed by SEM, and the grain size was 1.2 ± 0.4 μm. The dielectric properties were compared with those of the air-sintered $BaTiO_3$ ceramics with a grain size of 1.2 μm. Formulated $BaTiO_3$ ceramics, which fulfill X7R specifications, were prepared using a $BaTiO_3$-based powder (EV540N, Ferro, Cleveland, OH, USA). The compact of the $BaTiO_3$-based powder was sintered at 1,300 °C for 2 h in the air (10^{-2} atm pO_2) or at 10^{-9} atm pO_2[24]. No reoxidation post-annealing was performed. Figure 1C and D shows the SEM images of the formulated $BaTiO_3$ ceramics. Two formulated $BaTiO_3$ ceramics had the same grain size of 0.5 ± 0.2 μm. The thickness of both undoped and formulated $BaTiO_3$ ceramics was about 0.5 mm. For dielectric measurements, 100 nm thick Au electrodes were formed by sputtering. The details of the sample preparation and additional electric data are described elsewhere[24,25].

The grain size effect was also studied for model multilayer ceramics capacitors (MLCCs). The size of model MLCCs was 3.2 mm × 1.6 mm × 0.4 mm, and they consisted of ten 7.7-μm-thick $BaTiO_3$-based dielectric layers with X7R specifications and Ni internal electrodes. The grain sizes of the dielectrics were changed from 0.28 ± 0.1 μm, 0.36 ± 0.1μm, and 0.39 ± 0.1 μm by changing the sintering temperature, while the composition of the dielectrics was held constant. The details for the model MLCCs can be found in Refs.[26,27].

Measurement methods

For the undoped and formulated $BaTiO_3$ ceramics, the ac field dependence of the dielectric properties was measured using a lock-in amplifier (SR830, Stanford Research Systems Inc., Sunnyvale, CA, USA), a voltage
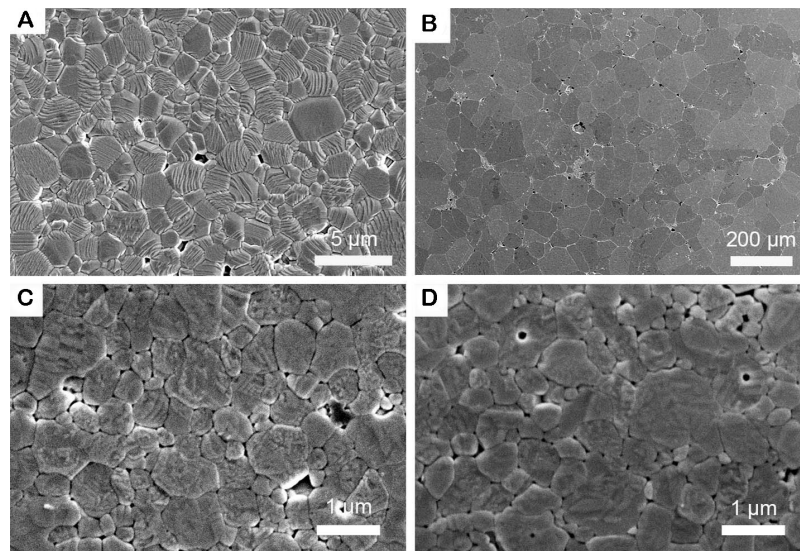
Figure 1. SEM images for undoped $BaTiO_3$ ceramics with grain sizes of (A) 1.2 μm and (B) 76 μm and formulated $BaTiO_3$ ceramics sintered at (C) 10^{-2} atm pO_2 and (D) 10^{-9} atm pO_2.

amplifier, and a charge converter[24]. An ac field frequency of 100 Hz was utilized. The ac field amplitude was increased up to 4 kV/cm; the coercive fields are 4 kV/cm for air-sintered undoped $BaTiO_3$ ceramics with 1.2 μm and 76 μm grain sizes, 3 kV/cm for undoped $BaTiO_3$ ceramics sintered at 10^{-9} atm pO_2 with a 1.2 μm grain size, and 5 kV/cm for formulated $BaTiO_3$ ceramics. The coercive fields were determined from polarization - electric field (P-E) loops measured by a custom-made measurement system at room temperature, as shown in Figure 2.

For the model MLCCs, the ac field dependence of the dielectric properties was measured using an LCR meter (4284A, Agilent Technologies Inc., Santa Clara, CA) with a frequency of 1 kHz. The ac field amplitude was increased up to 12-15 kV/cm. The coercive fields of the samples were about 10-15 kV/cm.

The temperature dependence of the dielectric properties was measured upon cooling from 150 °C to -150 °C or -180 °C, and the temperature of the samples was controlled by a furnace (DELTA 9023, Delta Design, Poway, CA); the chamber was cooled with liquid nitrogen. The dielectric data were measured on cooling to reduce artifacts associated with condensed moisture.

RESULTS AND DISCUSSION

Figure 3 illustrates the temperature dependence of the relative permittivity (ε') (prime) of a $BaTiO_3$ ceramic sample as a function of ac field amplitude. Several points are immediately apparent. First, at temperatures well above the Curie temperature T_c ~125 °C (i.e., measurements at 150 °C), where there should be no ferroelectric domains, there are no domain wall contributions to the properties. As a result, the dielectric permittivity shows very limited dependence on the amplitude of the ac electric field. As the temperature drops to the Curie temperature (data at 125 °C), it is apparent that there is a finite field dependence of ε', which may be due to persistent micropolar regions[28]. Below T_c in the tetragonal ferroelectric regime (data at 80 °C), there is a large population of mobile ferroelectric domain walls in the ceramics, and the nonlinearity in ε' increases. Near any of the phase transitions (apparent as peaks in the permittivity data), both the intrinsic polarizability and the domain wall contributions to the properties rise. The latter is clearly apparent as enhanced dielectric nonlinearity (for example, the data set at 20 °C). Substantial dielectric
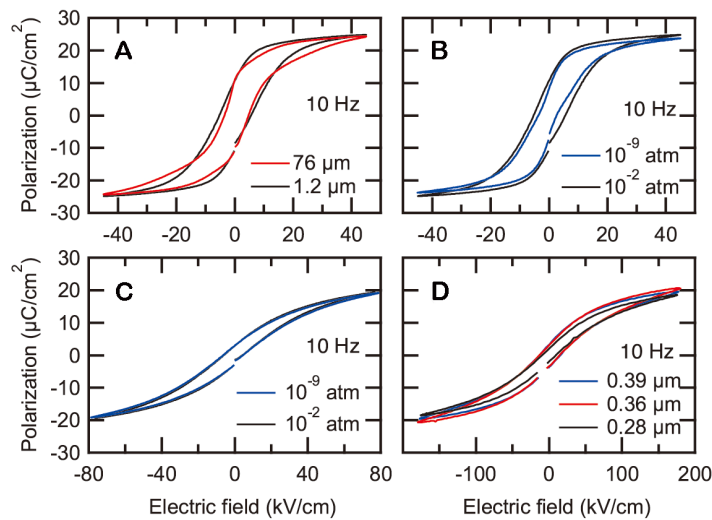
Figure 2. P-E loops measured at room temperature for (A) undoped $BaTiO_3$ ceramics with a grain size of 1.2 μm and 76 μm, (B) undoped $BaTiO_3$ ceramics sintered at 10^{-2} atm pO_2 and 10^{-9} atm pO_2, (C) formulated $BaTiO_3$ ceramics sintered 10^{-2} atm pO_2 and 10^{-9} atm pO_2, and (D) model MLCCs with various grain sizes. The ac frequency was 10 Hz.
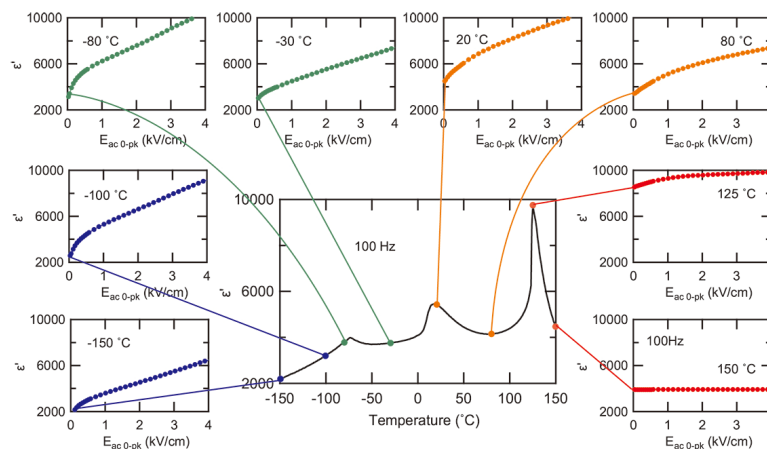

Figure 3. Temperature and the ac field dependence of the dielectric constant of a $BaTiO_3$ ceramics with a grain size of 1.2 mm. The ac field frequency was 100 Hz. The peaks in the permittivity correspond to the phase transition in $BaTiO_3$; on increasing temperature, the material transforms from a rhombohedral ferroelectric to an orthorhombic ferroelectric to a tetragonal ferroelectric to a paraelectric cubic structure.

nonlinearity is observed in the rhombohedral, orthorhombic, and tetragonal ferroelectric phases of $BaTiO_3$. Although not shown here, the domain wall motion contributions to the small signal properties are gradually lost as the temperature approaches 0 K[29].

The magnitude of the temperature dependence of the extrinsic contributions to the properties is a function of the grain size of the ceramics, as can be seen in comparing the data in Figures 3-5 (Figure 3 uses the same data as Figure 5, and Figure 5 has more data). Figure 4 shows selected data for the dielectric nonlinearity for a large-grained (76 mm average grain size) $BaTiO_3$ ceramics. One consequence of the increased domain wall mobility in large-grained materials is that the electric fields at which the materials transition from Rayleigh-

like to non-Rayleigh-like behavior decreases. As a result, Figure 4 shows marked departures from Rayleigh-like behavior at ac field magnitudes under 1 kV/cm in the tetragonal phase field for the $BaTiO_3$. Above these fields, the permittivity first rises very quickly as new domains are nucleated and then goes through a maximum before decreasing as the field amplitude is further increased. This is in contrast to the data in Figures 3 and 5 for finer-grained ceramics, where no marked maximum in the relative permittivity is observed up to 4 kV/cm over the same temperature range.

Figure 5 shows the ac field dependence of the dielectric properties of the undoped $BaTiO_3$ ceramics with a grain size of 1.2 μm measured at various temperatures. It was observed that the ac field dependence was suppressed compared to the large-grained sample over the whole temperature range, as has been reported elsewhere[23]. Grain boundaries are regions where the crystallography of the material is disrupted, and in many cases, these grain boundaries act as pinning centers for the domain walls[25,30-33].

The dielectric data for samples with different grain sizes were quantified by a pseudo-Rayleigh analysis that replaced ε_{init}' with ε_j' - the dielectric constant measured at a small field amplitude j. α' was replaced with α_i' - the slope for the dielectric constants measured at the field amplitudes j and i (i > j). In this case, pseudo refers to the fact that the permittivity does not increase truly linearly as a function of ac field. Figure 6 shows the temperature dependence of the pseudo-Rayleigh parameters of the $BaTiO_3$ ceramics with a grain size of 1.2 μm and 76 μm. The field i was chosen to ~0.5 kV/cm or ~2 kV/cm to quantify domain wall contributions at subcoercive fields. The temperature dependence of the $\varepsilon_{0.03kV/cm}'$ was similar to that of the small signal dielectric constant, except that no dielectric peak was observed at 125 °C for the large-grained ceramics due to its higher T_c of 128 °C[25]. The observation that the $\varepsilon_{0.03kV/cm}'$ of the 1.2 μm grain size sample is larger than that of the 76 μm grain size sample below T_c is due to the so-called grain size effect of $BaTiO_3$[7]. For the 76 μm grain size sample, the α_i' values were larger than those of the 1.2 μm grain sample due to reduced domain wall pinning at grain boundaries. The α_i' values were increased at the rhombohedral to orthorhombic phase transition and orthorhombic to tetragonal phase transition temperatures. In addition, they were increased at 80 °C for the 76 μm grain size sample. This is probably due to a combination of increased domain wall mobility and decreased polarization with increasing temperature. For the 1.2 μm grain size sample, the increases at 80 °C were not observed due to suppressed domain wall mobility. For the 76 μm grain size sample, $\alpha_{2kV/cm}'$ is larger than $\alpha_{0.5kV/cm}'$ above -70 °C, indicating a superlinear ac field dependence. This, in turn, suggests a sublinear response below this temperature, which would be consistent with a restriction in long-range domain wall motion and/or a reduction in the nucleation of new domains.

Given that domain wall motion is a function of the concentration of pinning sites in the sample, it is also interesting to consider the effect of point defects as potential pinning points. Here, the oxygen vacancy concentration was varied by sintering undoped $BaTiO_3$ ceramics at different oxygen partial pressures, as described elsewhere[24]. Figure 7 shows the ac field dependence of the dielectric properties of $BaTiO_3$ ceramics sintered at 10^{-9} atm pO_2 with a 1.2 μm grain size measured at various temperatures. It was found that the response was similar to that of the sample sintered at 10^{-2} atm pO_2, except that the larger increase in the dielectric properties at moderate ac fields than that of the sample sintered at 10^{-2} atm pO_2 below T_c and larger loss above T_c.

The effect of the pO_2 on the dielectric nonlinearity was quantified at various temperatures, as shown in Figure 8. Neither sample showed a true Rayleigh regime, presumably due to a combination of defect dipoles associated with oxygen vacancies, residual stresses[34], and pinning from the grain boundaries. It was found that the temperature dependence of the pseudo-Rayleigh parameters was similar, except that the α_i' of 10^{-9} atm pO_2 sample were larger than those of the 10^{-2} atm pO_2 sample, which is attributable to the de-
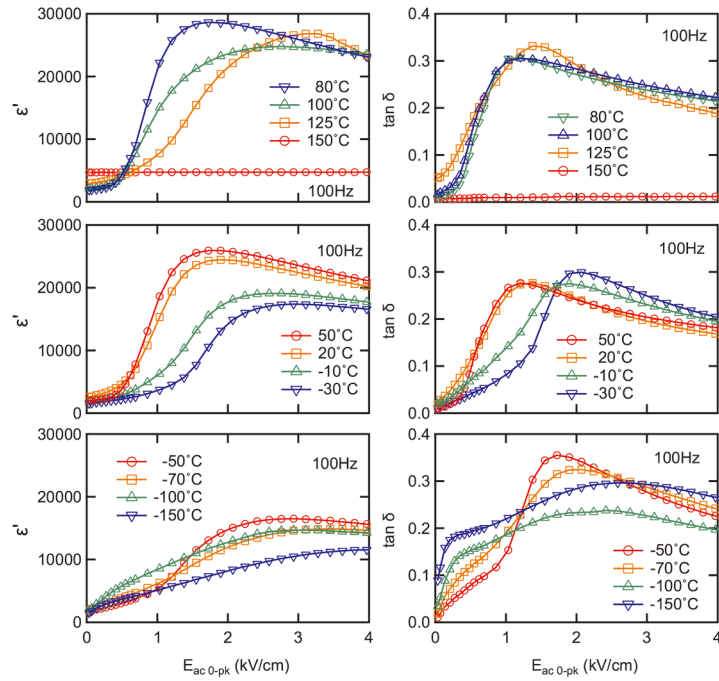
Figure 4. The ac field dependence of the dielectric properties of undoped BaTiO$_3$ ceramics with a grain size of 76 μm measured at various temperatures.
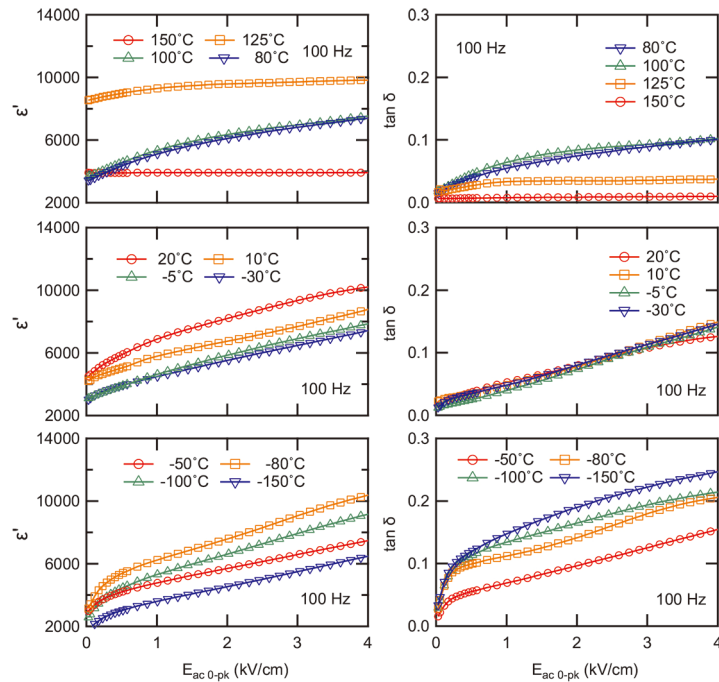

Figure 5. The ac field dependence of the dielectric properties of undoped BaTiO$_3$ ceramics with a grain size of 1.2 μm, measured at various temperatures.
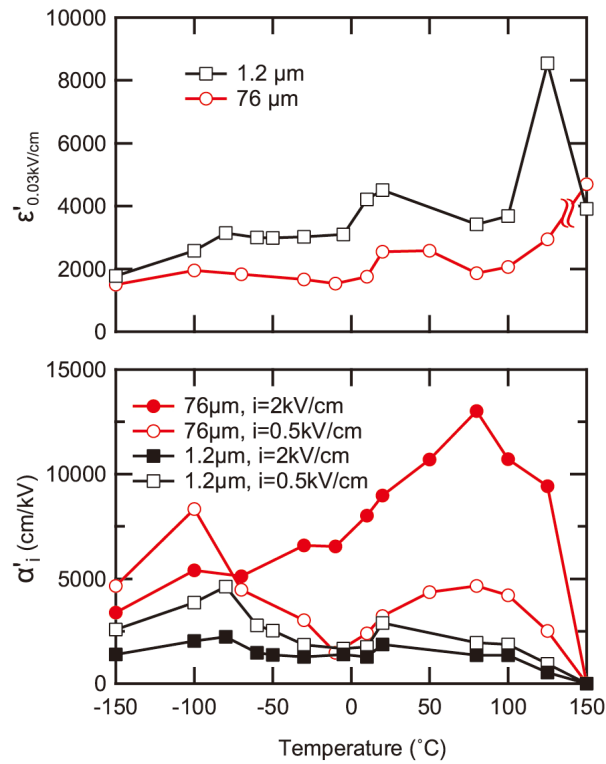
Figure 6. Temperature dependence of the pseudo-Rayleigh parameters of the BaTiO$_3$ ceramics with grain sizes of 1.2 µm and 76 µm.
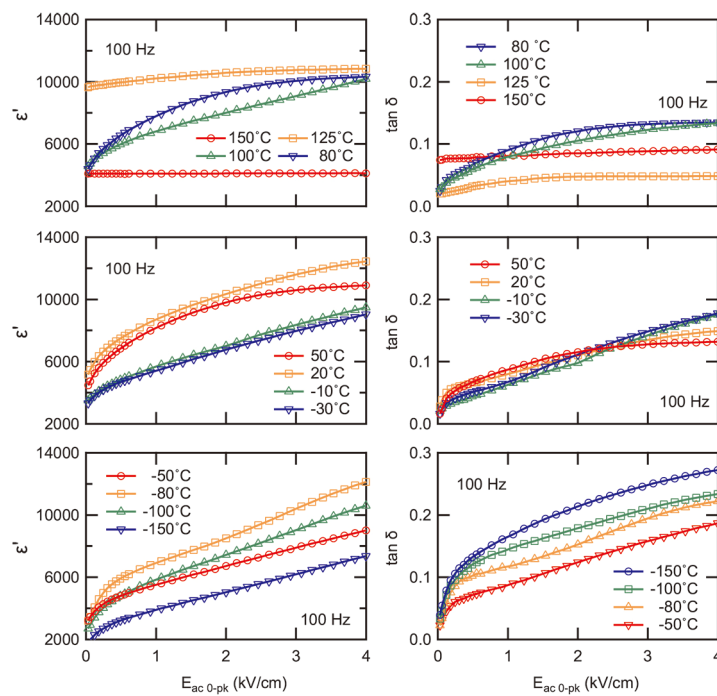

Figure 7. The ac field dependence of the dielectric properties of the undoped BaTiO$_3$ ceramics sintered at 10^{-9} atm pO$_2$ measured at various temperatures.
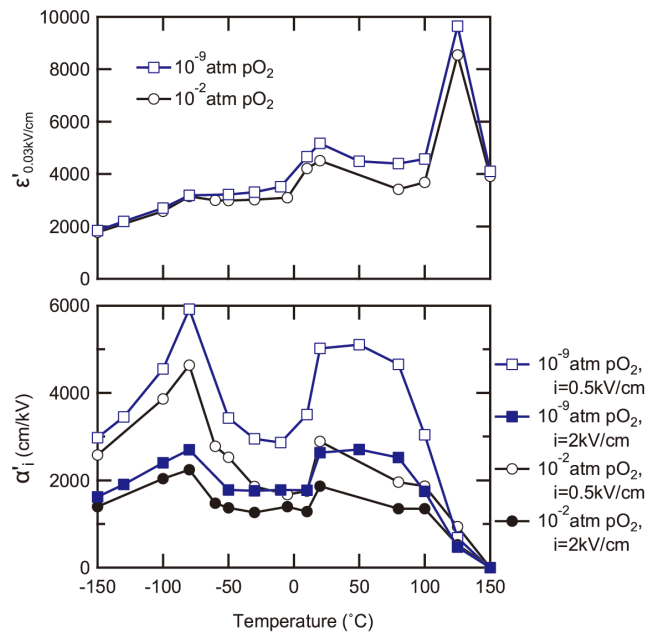
Figure 8. Temperature dependence of the pseudo-Rayleigh parameters of the BaTiO$_3$ ceramics sintered at 10^{-9} atm pO$_2$ and the BaTiO$_3$ ceramics sintered at 10^{-2} atm pO$_2$ and post-annealed.

pinning of domain walls from weak pinning centers associated with the defect dipoles[24].

In most multilayer ceramic capacitors, the BaTiO$_3$ is formulated to reduce the temperature dependence of the permittivity and increase the reliability when base metal electrodes are utilized[35]. It is thus interesting to compare the temperature dependence of the extrinsic contributions of a formulated dielectric to that of undoped ceramics. Figure 9 shows the ac field dependence of the dielectric properties of formulated BaTiO$_3$ ceramics sintered at 10^{-2} and 10^{-9} atm pO$_2$; these samples showed core-shell microstructures[24]. Above T$_c$, the dielectric constant of both samples was independent of pO$_2$; the permittivities of the two samples were nearly identical in this regime due to the similar grain sizes (both samples had grain sizes of ~0.5 μm) and the absence of a large concentration of mobile interfaces. As expected, provided that the samples are far enough above T$_c$, there are few residual micropolar regions, and the nonlinear dielectric response of formulated and undoped ceramics is similar. In contrast, below T$_c$, the irreversible contributions to the permittivity were substantially suppressed in the formulated ceramics relative to the undoped materials. At 20 °C, the ac field dependence of the 10^{-2} atm pO$_2$ sample was almost linear, while that of the 10^{-9} atm pO$_2$ sample was sublinear.

The dielectric responses were quantified using the pseudo-Rayleigh analysis, as shown in Figure 10. Below T$_c$, the $\varepsilon'_{0.03kV/cm}$ of the 10^{-2} atm pO$_2$ sample monotonically decreased with temperature, while that of the 10^{-9} atm pO$_2$ sample showed a core/shell response. This is consistent with the temperature dependence of the small signal dielectric permittivity of the samples[24]. With decreasing temperature, α'_i increased up to the orthorhombic to rhombohedral phase transition and then decreased, which is consistent with the α'_i for the small-grained undoped BaTiO$_3$ ceramics (although the increase at the tetragonal to orthorhombic phase transition was smeared). It was found that the difference of the α'_i between the formulated samples was small above the T$_c$ of the shell region. This suggests that the domain wall contributions are strongly influenced by the shell region. Note that near room temperature, $\alpha'_{2kV/cm}$ and $\alpha'_{0.5kV/cm}$ of the 10^{-2} atm pO$_2$ sample were similar, which corresponds to the Rayleigh behavior.

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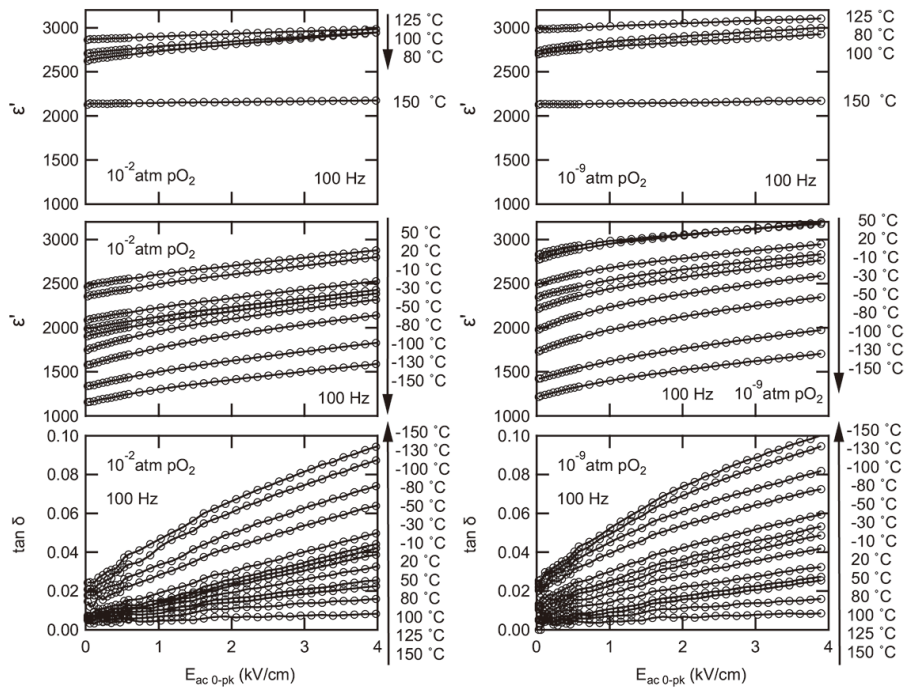
Figure 9. The ac field dependence of the dielectric properties of the formulated $BaTiO_3$ ceramics sintered at 10^{-2} atm pO_2 and 10^{-9} atm pO_2 measured at various temperatures.
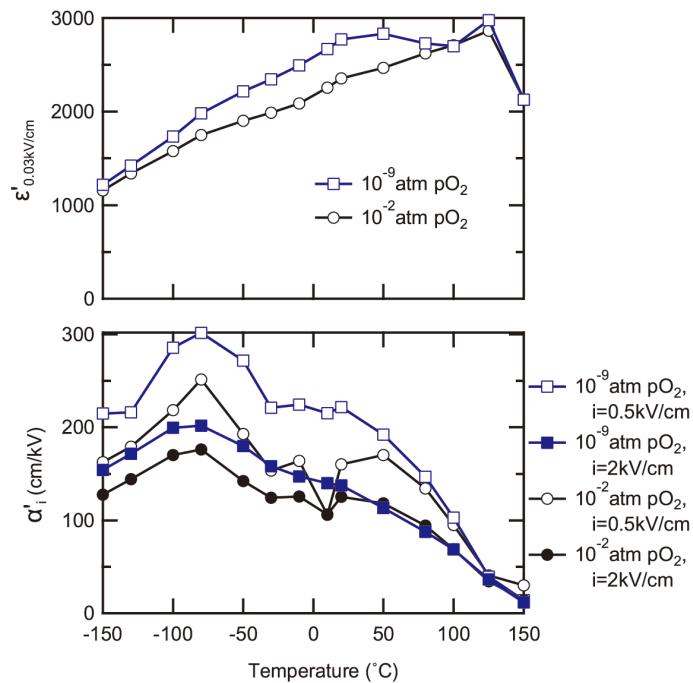
Figure 10. Temperature dependence of the pseudo-Rayleigh parameters of formulated $BaTiO_3$ ceramics sintered at 10^{-2} atm pO_2 and 10^{-9} atm pO_2.
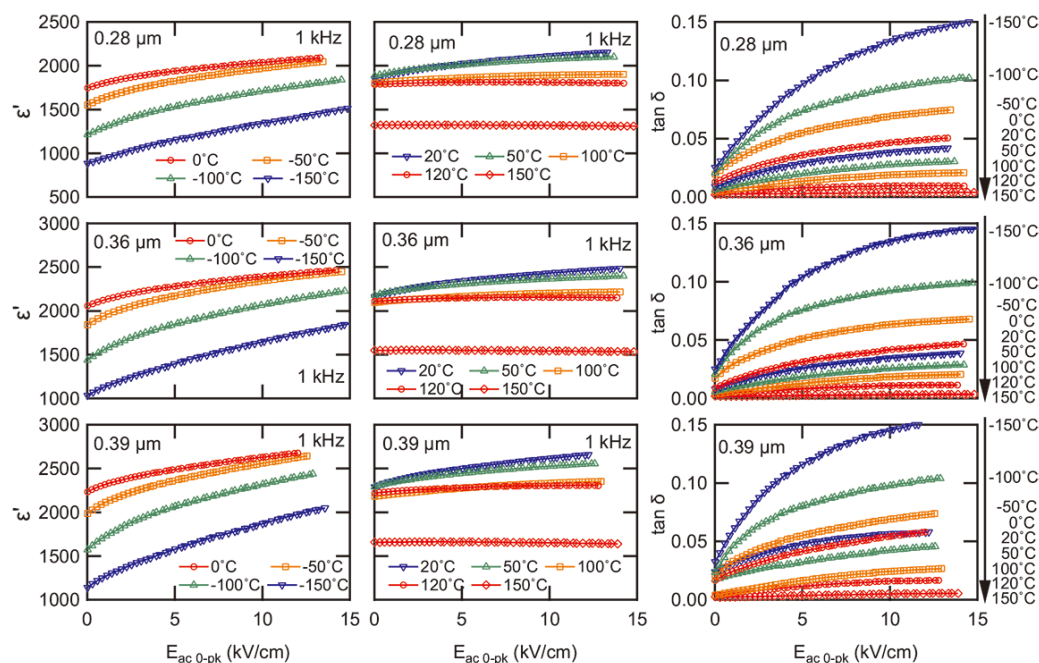
Figure 11. The ac field dependence of the dielectric properties of model MLCCs with different grain sizes measured at various temperatures.

It is also notable that the values for α'_i for these formulated $BaTiO_3$ ceramics are approximately an order of magnitude smaller than those of the undoped $BaTiO_3$ in the ferroelectric phases. There may be several reasons for this. First, the formulated ceramics had a small grain size of ~0.5 μm, which induced additional grain boundary dilution of the response. Secondly, the formulated $BaTiO_3$ has a lower volume fraction of the ferroelectric phase associated with the introduction of shell regions. These non-ferroelectric regions will also act as capacitors in series that suppress the extrinsic contributions to the response. Thirdly, it is also possible that the core-shell microstructures act to suppress the long coupling of the domain wall motion. It has been shown that domain walls often have some level of continuity across grain boundaries[36] and that the resulting ensembles of domain walls often move as clusters rather than as isolated walls[37,38]. It is not straightforward to separate the relative importance of each of these factors since the second and third, in particular, will also be functions of temperature themselves.

Figure 11 shows the ac field dependence of the dielectric constant for formulated $BaTiO_3$ MLCCs with various grain sizes measured at various temperatures. Above T_c, the dielectric constant was independent of the ac field amplitude. However, the permittivity data do not superimpose for the different grain sizes, presumably because of a difference in the grain boundary dilution of the response[39]. Below T_c, the dielectric constant depends on the ac field, and the ac field dependence increases with decreasing temperature. The ac field dependence was quantified using pseudo-Rayleigh analysis, as shown in Figure 12. The ε'_j followed a core/shell response of the dielectric constant. With decreasing grain size, the ε'_j decreased. The temperature dependence of the α'_i was similar to the formulated $BaTiO_3$ ceramics. The peak at the orthorhombic to rhombohedral phase transition decreased with grain size. This is consistent with the grain size dependence of the undoped $BaTiO_3$ ceramics. It was observed that the grain size dependence of α'_i was relatively weak above the T_c of the shell. This result is consistent with the pO_2 dependence of α'_i for the formulated $BaTiO_3$ ceramics, suggesting the influence of the shell region on irreversible domain wall contributions.
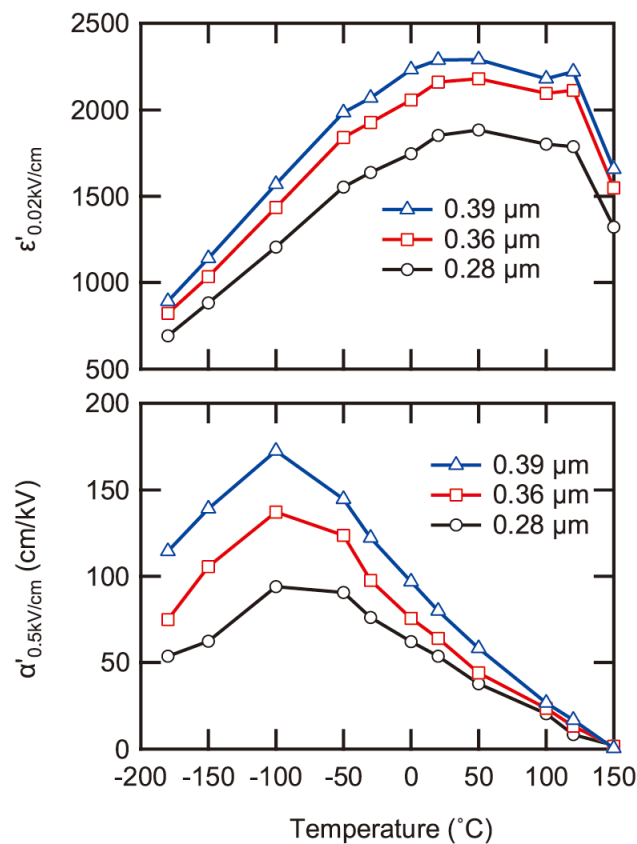
Figure 12. Temperature dependence of the pseudo-Rayleigh parameters of the MLCCs with various grain sizes.

CONCLUSIONS

In conclusion, this paper has demonstrated the temperature dependence of the extrinsic responses in both undoped and formulated $BaTiO_3$. Knowledge of this behavior is important to understand how the materials will perform in working conditions. Given that domain wall motion is thermally activated, it also depends on temperature. The relative magnitude of the extrinsic contributions to the properties is a strong function of the microstructure of the ceramics, especially the grain size and the existence of core-shell microstructures; it is a much weaker function of the concentration of oxygen vacancies.

DECLARATIONS

Acknowledgments

Authors' contributions
The conception and design of the work: Trolier-McKinstry S

The acquisition and analysis of data: Fujii I

The interpretation of data: Fujii I, Trolier-McKinstry S

The writing and revising: Fujii I, Trolier-McKinstry S

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