

Evidence of the Internal Domains for Inducing the Anomalously High Dielectric Constant of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$

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The delicate self-intertwined domain structures inside the grains of the polycrystalline $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) were discovered by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM), which provided a direct clue in understanding the mystery of the huge dielectric response of this intriguing material. Domain morphologies with and without terrace and ledge were observed by SEM. The detailed domain structures were further examined by HRTEM, and it was found that they contained strained and unstrained domains. The strained domains essentially are constructed by various dimensional superlattices. The coherent domain boundaries were considered to be strained, composition-disordered, and insulating. A microstructural model and its equivalent circuit based on a series connection with semiconducting domain interior, insulating domain boundary, and insulating grain boundary have been established, which not only solve the contradictory explanation of the dielectric response between polycrystalline and single-crystal CCTO but also provide a reasonable interpretation of the experimental results related to enhancement of the dielectric responses of CCTO.

I. Introduction

An unusual and promising ceramic material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) was recently found to possess an extraordinarily high dielectric constant at room temperature of about 10^4 – 10^5 , which is practically frequency independent between dc and 10^6 Hz and possesses good temperature stability over a wide temperature range from 100 to 600 K.^{1,2} Owing to these remarkable properties, CCTO is being considered as a very promising material for application in microelectronics, mainly in capacitive components. Understanding the mechanism of the underlying properties of CCTO ceramics and single crystals may lead to development of new high dielectric constant CCTO-based materials with a broad temperature- and frequency-independent dielectric response. For this reason, the mechanism for inducing the huge dielectric response of CCTO has been intensely investigated, which, however, so far still remains unresolved.

According to the structure analysis, the tilt of the TiO_6 octahedra is large enough to accommodate local distortions, which in turn would effectively rule out the pure ferroelectric behavior of CCTO.^{1,2} Indeed, no structural or ferroelectric transition was observed in CCTO in a wide temperature range.^{1,3} Moreover, in comparison with other isostructural compounds, only CCTO possesses much higher permittivity.¹ The intrinsic nature of the crystal has been questioned and essentially is contrary to the results based on the first-

principle calculations.^{4,5} Structural¹ and spectroscopic^{2,3,6,7} investigations of the dielectric responses of the polycrystalline and single-crystal CCTO suggested the interface was the main contribution. Recently, Tselev et al.⁸ found a low intrinsic dielectric constant of about 100 in an epitaxial thin-film CCTO and further provided evidence for an extrinsic and Maxwell–Wagner-type origin of the colossal dielectric response of CCTO.

For the extrinsic mechanism the barrier-layer model^{9–11} has been considered as the most favorable one to explain the giant capacitance behavior of both polycrystalline and single-crystal CCTO. The intrinsically conductive CCTO has been manifested by the recent confirmation of the three-dimensional variable range hopping conduction behavior⁸ and the Ti on Cu sites indirectly providing the charge carriers for the Ti 3d band.¹² However, the insulating layer was not well justified. Regarding the barrier layer of the single crystal, in addition to the locally planar twin boundary,¹ antiphase and compositional ordering domain boundaries were pro-

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posed.¹¹ The former, which was examined by X-ray,¹ was not fully justified, and recent detailed TEM studies did not reveal twin domains with a size larger than 10 nm in their CCTO films.⁸ The latter two, however, have not been observed so far. For the polycrystalline CCTO the insulating blocking layers were usually considered to be grain boundary.^{9,10,13–15} However, the origin of the grain boundary insulating barrier layer was still not justified. Moreover, it would be contradictory for the giant dielectric response of CCTO to have the dielectric-response mechanism with different kinds of the origins, namely, the internal boundaries for the single crystal but the grain boundaries for the polycrystal. Though the contact contribution to the dielectric response of the CCTO^{16,17} may avoid this contradiction, there are two main reasons to consider that it is not related to the anomalously high dielectric constant of CCTO. First, the complex impedance analysis clearly evidenced that the giant dielectric response arose from the internal domains or the grain boundaries of the ceramic CCTO.^{9,10,18} Second, the dielectric response was dependent of the porosity, microstructure, and Cu stoichiometry.^{1,18,19}

The recent discovery¹⁸ of internal domains inside the grains has indeed solved this contradiction, which also strongly suggested that the huge dielectric response of CCTO be extrinsic and its origin related to the barrier layer mechanism. Nevertheless, the formation mechanism and detailed structures and properties of the domains have not yet been clarified. In this investigation the detailed domain structures have been explored and provide deep insight into the mechanism for inducing the anomalously high dielectric constant of ceramic CCTO. Moreover, a microstructural model and its equivalent circuit for enhancement of the colossal dielectric response of CCTO have also been established.

II. Experimental Section

Appropriate amounts of high-purity CaCO₃, CuO, and TiO₂ reagents were used to prepare CCTO. They were mixed in a ball mill with ZrO₂ balls for 12 h. After drying, the powder was calcined for 2 h at 950 °C in air and then milled again for 12 h. The powder was then pressed in an 11 mm diameter steel die. Pellets were sintered at 1065 °C in air for different times and then furnace-cooled to room temperature. Sintered pellets were cut, polished, and thermally etched for microstructural observation. The thermal etching can be considered to develop the so-called “grain boundary groove”,²⁰ and the etching rate depends on the boundary energy. Scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) were used to analyze the

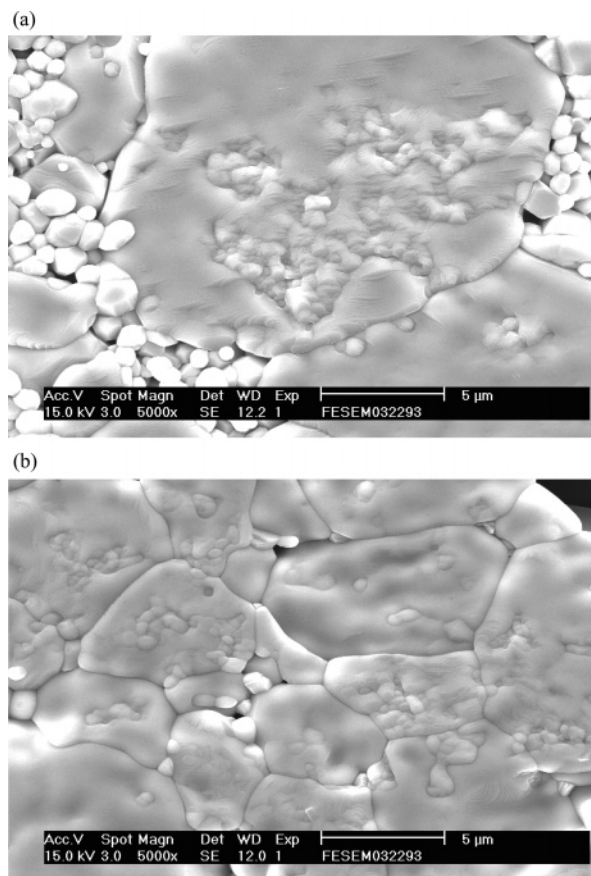


Figure 1. SEM micrographs for the CCTO sintered at 1065 °C for (a) 4 and (b) 20 h, under thermal etching condition at 960 °C for 72 min, showing the domains with and without terrace–ledge morphology inside the grain.

microstructures and domain structures. Impedance measurements were performed at 1 V over a frequency range from 20 Hz to 1 MHz using a precision LCR meter.

III. Results and Discussion

Figure 1 shows SEM micrographs of the samples sintered at 1065 °C for 4 and 20 h. Under the thermal etching conditions at 960 °C for 72 min, domain morphologies with and without terrace and ledge were observed. The terrace–ledge morphology was speculated to be induced by the dislocations, similar to the spiral growth of the crystal via the screw dislocation. Actually, it has been evidenced in Figure 2 that there are orderly arranged dislocations inside the grain. On the basis of Figure 1 and the microstructural evolution shown in previous work,¹⁸ the domains were scarcely observed in the fine grains (<2 μm) but were apparently revealed inside the abnormal large grains for the long-time sintered samples. Figure 3 shows the detailed domain structures and the diffraction pattern. The grain interior was found to be intertwined with dark and bright domains. The dark domains were further analyzed, and it was found that they consist of finer structures with various dimensional superlattices. They have been further justified by the electronic diffraction pattern of [001] zone axis with streaks cutting through each diffraction spot, and the streaks are essentially comprised of various closely spaced extra diffraction spots. Because the superlattices had various dimensions, the strain would be present inside the ordered microdomains, which is the reason this type of domain

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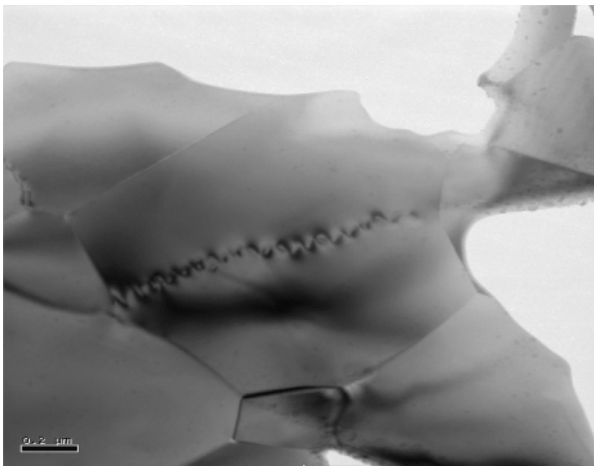


Figure 2. HRTEM micrograph for the CCTO sintered at 1065 °C for 4 h showing the orderly arranged dislocations inside the grain.

reveals darkness in the HRTEM micrograph. Moreover, the superlattices seem to be preferentially oriented along the [200] direction. Furthermore, because CCTO was suggested to be Cu deficient,^{18,19} the superlattices could be formed via the ordering of the Cu vacancies, analogous to the Brownmillerite structure constructed by oxygen-vacancy ordering.²¹

On the basis of the observation of the domain structures in Figure 3, the boundaries between strained and unstrained domains are not only strained due to the lattice coherency but also composition-disordered. A recent report by Tselev et al.⁸ suggested that the conduction mechanism of CCTO could be pictured as the hopping charge carriers confined within small domains; therefore, the strained and composition-disordered domain boundaries could make up large energy barriers for hopping and be assumed to be insulating. On the basis of the SEM and HRTEM micrographs, the microstructural model for enhancement of the dielectric response of CCTO can be established and has been schematically illustrated in Figure 4a. This microstructural model essentially can be simulated by a brick-layer model,²² treated as an array of cubic-shaped domains separated by flat domain and grain boundaries. The current flow is assumed to be one-dimensional, and the curvature of the current paths at the corners of the domains is neglected. In this case, there are three paths available to the current, namely, across domains—domain boundaries—grain boundaries, along domain boundaries, or along grain boundaries. While the domains were suggested to be conductive, the conductivity of the domain boundary and grain boundary still needs to be realized. The resistivity of the grain boundary may be determined by microcracks, mismatch of the lattices, segregation, space charge, or a combination of these factors. For very high purity ceramics it was estimated that the resistivity of the grain boundary was about 100 times higher than that of the bulk.²³ Because the resistivity of the domain or grain interior of CCTO was estimated to be $<10^3 \Omega \text{ cm}$,¹⁸ the grain boundary resistivity without impurity segregation would be

$<10^5 \Omega \text{ cm}$. The domain boundaries were suggested to be developed between strained and unstrained domains, which include the lattice mismatch and chemical ordering. Thus, it is expected that the resistivity of the domain boundary would not differ from that of the grain boundary by 1 order of magnitude. Obviously, the resistivity of the domain interior would be much lower than that of the domain boundary or grain boundary. Therefore, the conduction path along the domain boundaries or grain boundaries is negligible, and the conduction path through the domains and across domain boundaries and grain boundaries dominates. This series-connected conduction path can be simulated by the equivalent circuit of Figure 4b, and the bulk conduction behavior can best be described in terms of complex resistivity. On the basis of Figure 4b, the total bulk resistivity (ρ_t) of the whole sintered body can be expressed as

$$\rho_t = \rho_g + (x_{\text{db}}/3)\rho_{\text{db}} + (x_{\text{gb}}/3)\rho_{\text{gb}} \quad (1)$$

where x_{db} and x_{gb} are the volume fractions and ρ_{db} and ρ_{gb} are the resistivities of domain boundaries and grain boundaries, respectively. On the basis of the microstructural evolution, the weight of the domain-boundary resistivity will essentially increase but that of the grain-boundary resistivity will decrease due to growth of the grains during the sintering process. However, the grain-boundary resistivity would be greatly enhanced when impurity segregates to the grain boundaries. As discussed above, without impurity segregation the resistivity of the domain boundaries and grain boundaries is around $10^5 \Omega \text{ cm}$. Thus, the higher evaluated total bulk resistivity of $>10^5 \Omega \text{ cm}$ shown in the previous work¹⁸ would indicate that there was impurity segregation to the grain boundary.

Complex impedance analysis has been known to be able to distinguish the resistance between grain and grain boundary. On the basis of the aforementioned discussion, the equivalent circuit is in series with the parallel RC elements of domain, domain boundary, and grain boundary shown in Figure 4b. According to the impedance analysis theory,²⁴ the position of the arcs in the frequency spectrum depends on their relaxation time τ , where $\tau = RC$ (R , resistance; C , capacitance), because at the arc maximum the relationship $\omega_{\text{max}}RC = 1$ holds, where ω is the angular frequency ($=2\pi f$, f is the applied frequency, in Hz). To distinguish the impedance spectrum of the components in the equivalent circuit, the time constant τ must differ by at least 2 orders of magnitude. Moreover, the samples must possess adequate resistivity; otherwise, the spectrum features will collapse into the origin of the complex impedance plot. The semiconductive grain interior would be the case. However, for the rest of the series connection of the parallel RC elements of the grain boundary and the domain boundary, the complex impedance plot, in principle, should reveal two semicircles. Figure 5 shows the complex impedance plane and modulus spectrum of CCTO sintered at 1065 °C for 20 h, and a measuring temperature of 55 °C was selected for the illustration. As observed in Figure 5a, the complex impedance plane revealed one semicircle. There are two situations to reveal one semicircle, namely, the difference of RC values

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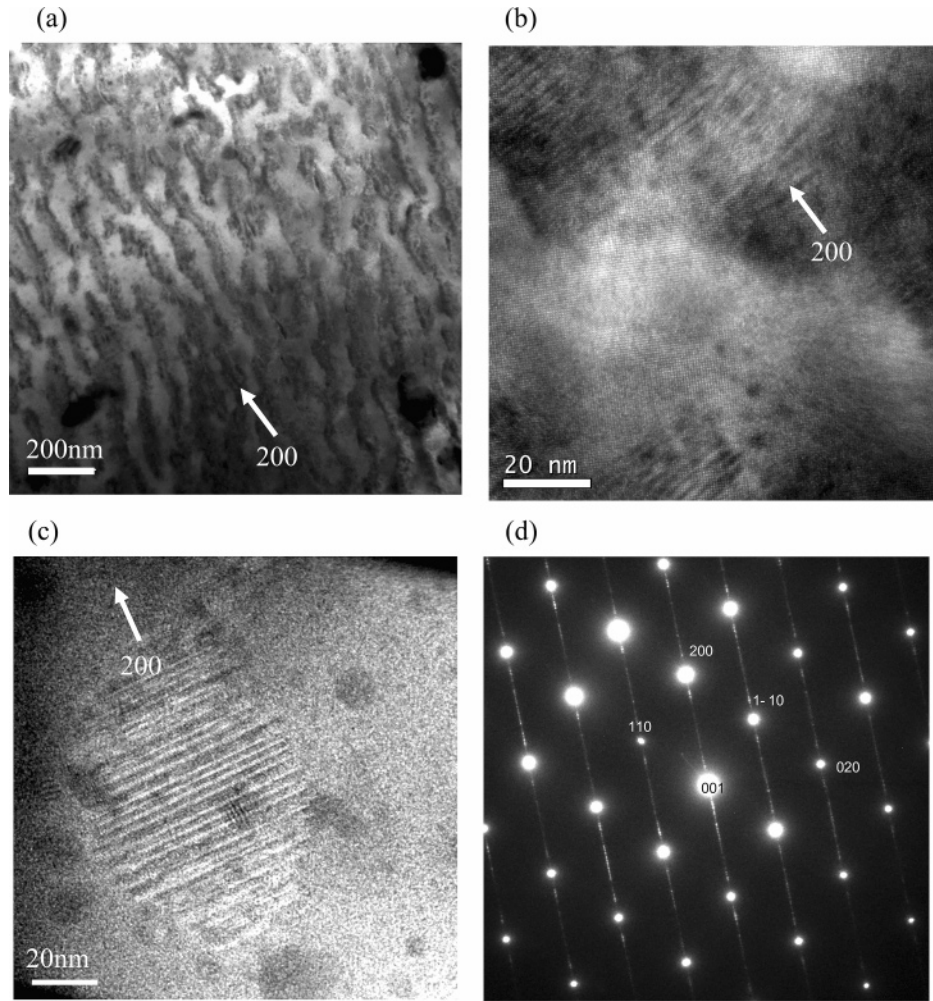


Figure 3. HRTEM micrographs and diffraction pattern for the CCTO sintered at 1065 °C for 20 h showing (a) the grain interior with intertwined dark and bright domains, (b) higher magnification of a revealing that dark domains possess a finer structure, (c) the finer structure inside dark domains revealing the various dimensional superlattices, and (d) the diffraction pattern of the superlattices revealing the streaks with various dimensional spaces.

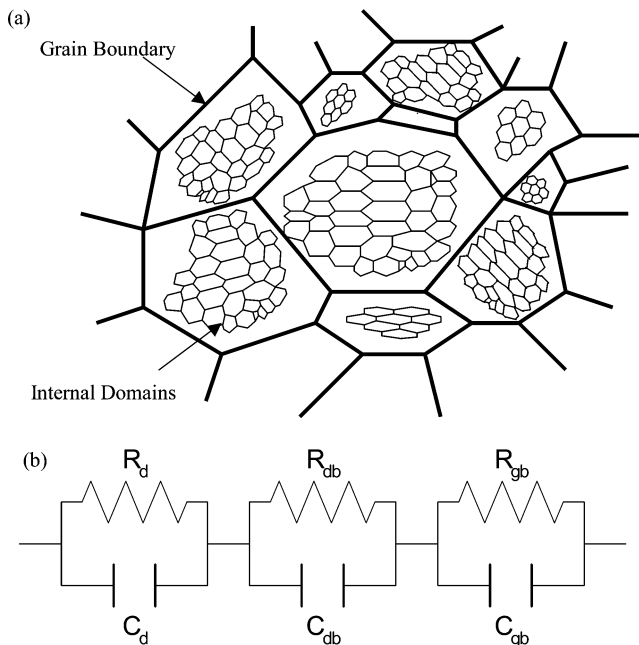


Figure 4. Microstructure model of polycrystalline CCTO showing the internal domains inside the grains. (b) Equivalent circuit of a. R_d , R_{db} , and R_{gb} are the resistance of domain, domain boundary, and grain boundary, respectively. C_d , C_{db} , and C_{gb} are the capacitance of domain, domain boundary, and grain boundary, respectively.

is less than 2 orders of magnitude and the resistance of one of the RC elements is very high and out of the measured range. Inferring from the aforementioned discussion, the former would be more probable and may be distinguished by the modulus spectrum. For the spectrum of Z'' or M'' versus $\log f$, each parallel RC element results in a Debye peak in each spectroscopic plot. The Debye peak in the Z'' or M'' spectrum is described, respectively, by²⁴

$$Z'' = R[\omega RC/(1 + (\omega RC)^2)] \quad (2)$$

$$M'' = C_o/C[\omega RC/(1 + (\omega RC)^2)] \quad (3)$$

where C_o is the vacuum capacitance of the measuring cell and electrodes with an air gap in place of the sample. $C_o = \epsilon_o A/d$, where ϵ_o the permittivity of free space, 8.854×10^{-12} F m⁻¹, d is the thickness, and A is the area. Consequently, the Z'' spectra are dominated by those RC elements with the largest R values, whereas the M'' spectra are dominated by those with the smallest C values. The magnitudes of M''_{\max} and Z''_{\max} at the peak maxima are given by

$$Z''_{\max} = R/2 \quad (4)$$

$$M''_{\max} = C_o/2C \quad (5)$$

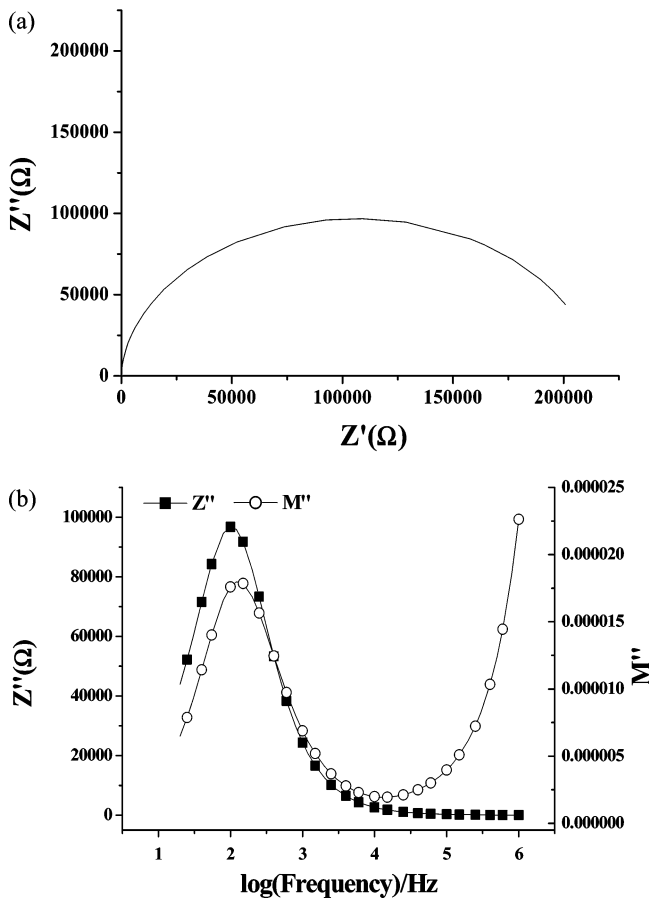


Figure 5. (a) Z^* complex impedance plane, and (b) Z'' and M'' spectroscopic plots at 55 °C of CCTO sintered at 1065 °C for 20 h.

In Figure 5b, though there are two peaks appearing, the high-frequency peak at 10⁶ Hz is attributed to the grain interior because the capacitance is very low. In addition, on the basis of eqs 4 and 5, the values of $R = 1.94 \times 10^5 \Omega$ and $C = 7.15 \text{ nF}$, corresponding to a dielectric constant $k = 27832$, can be derived from the low-frequency peak. However, at this stage we cannot assign these RC values to domain boundary or grain boundary.

On the basis of Figure 4 showing the microstructural model and the equivalent circuit, both the domain boundary and grain boundary, in principle, would contribute to the anomalously high dielectric response of CCTO. According to the brick-layer model of the barrier-layer capacitor,²² the dielectric response of the polycrystal or the single crystal can be estimated. The effective dielectric constant ϵ_{eff} of the microstructure with the domains and domain boundaries can be expressed as $\epsilon_{\text{eff}} = \epsilon_d t_d / t_{\text{db}}$, where ϵ_d is the dielectric constant of the domain interior and t_d and t_{db} are the thickness of the domain and domain boundary, respectively. On the basis of the SEM observation of the internal domains, the domain size is about 0.2–0.5 μm . Because the domain boundary is coherent between strained and unstrained domains, the effective thickness affected by the compositional disordering could be estimated about 1–5 atomic sizes, i.e., 0.2–1 nm. If so, ϵ_{eff} would be about 10^4 – 10^5 when ϵ_d is about 100, which is consistent with the experimental values of CCTO. For the microstructure with the grains and grain boundaries, the effective dielectric constant ϵ_{eff} can be expressed as $\epsilon_{\text{eff}} = \epsilon_g t_g / t_{\text{gb}}$, where ϵ_g is the dielectric constant

of the grain interior and t_g and t_{gb} are the thickness of the grain and grain boundary, respectively. In view of the microstructural model shown in Figure 4a, the effective volume of the grain will be reduced about 1 order of magnitude when the domains are present inside the grain. Therefore, the effective dielectric constant would be around 10^3 – 10^4 . For the fine grains without domains inside, the effective dielectric constant was also estimated to be around 10^3 – 10^4 .¹⁹ However, it should be noted that for polycrystalline CCTO the grain boundaries would become dominant in inducing the giant dielectric response when the grain-boundary barrier thickness is thin enough.^{19,25}

Furthermore, the polycrystalline CCTO can be considered as a composite of each grain because the dielectric constant of the individual grain is different. Therefore, the overall effective dielectric permittivity could be reasonably estimated by the so-called logarithmic mixture rule.²⁶ Therefore, the value of the effective dielectric constant of polycrystalline CCTO is, in general, lower than that of the single crystal. This is supported by previous work,¹⁸ showing that the dielectric constant increased with the volume fraction of the abnormal large grains. Finally, because of the observation of the detailed domain structure, several things can be interpreted. First, the orderly arranged dislocations could only be developed during the transition period of the order–disorder transformation of the superlattices. Thus, for the long-time sintered samples, the dislocation density would be lowered, which in turn would make the appearance of the terrace–ledge morphology less. Second, the domains were scarcely developed inside the fine grains,¹⁸ which could be attributed to their high strain energy. Finally, because the energy of the strained coherent domain boundary is lower than that of the grain boundary, it provides the reason that the thermal etching conditions for development of the domain boundaries required higher temperature and longer time.¹⁸

IV. Conclusions

Domain structures have been discovered inside the grains in which there are two kinds of domains, namely, strained and unstrained domains. The former was found to be constructed by various dimensional superlattices. The coherent domain boundaries between the strained and unstrained domains were expected to be strained, composition disordered, and insulating. The established internal barrier-layer model and its equivalent circuit shown in Figure 4 have provided a sound interpretation of most of the experimental results related to the giant dielectric response of CCTO. The discovery of the internal domains inside the grains of the polycrystalline CCTO not only solves the contradictory explanation of the dielectric response between polycrystalline and single-crystal CCTO, but also justified the extrinsic effect of the enhancement of the dielectric response of CCTO.

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