Reply to Comment on "Origin of Giant Dielectric Response in Nonferroelectric $CaCu_3Ti_4O_{12}$: Inhomogeneous Conduction Nature Probed by Atomic Force Microscopy"

In his comment, Chung argues our interpretation of *intragrain* boundary effects on the giant dielectric response in $CaCu_3Ti_4O_{12}$ (CCTO)[1] and claims that our explanation of the *percolative network* formed by the conductive regions in polycrystals to the network of grain boundaries on the basis of local current probing and scanning electron microscopic measurements are "seriously misleading and inaccurate". His comments are made from the following unreasonable claims: (1) the width of our observed conductive boundary (~100 nm) is larger than a grain boundary of "a few nanometers" given by the author. (2) Sample B annealed by the floating-zone method in our paper is not in a thermodynamically equilibrium state. (3) Our theoretical model does not give a correct estimation to the insulating regions from the current images. These unsubstantiated claims are possibly derived from a complete misunderstanding of our paper by the author.

Since the first report by Subramanian et al.,[2] giant dielectric responses up to 10^5 in CCTO have been observed for both the samples of polycrystals[3] and single crystals.[4] Because either precise structural analysis[2,5] or the first principles calculation[6] indicate that the nonpolar structure with a centro-symmetry is stable for CCTO, it is generally accepted that such a giant response has an extrinsic nature of an interface barrier effect as described in the textbook of Maxwell[7] and the paper of Wanger.[8] There are two possible sources of the barriers: (1) the barrier layers between the insulating *grain boundaries* and the semiconducting grains as the case of barrier layer capacitor[9] or (2) the *intragrain* insulating barrier layers.[10] As pointed out by Cohen et al. in their theoretical analysis,[11] both models can reasonably explain the observed giant dielectric responses in CCTO polycrystals, but the insulating *grain boundary model* cannot explain the extremely large dielectric constant observed in single crystal without grain boundary. It is no wonder that both models remain to be confirmed by the local probing techniques such as atomic force microcopy (AFM). Chung et al. indeed demonstrated the presence of the potential barrier in CCTO polycrystals by scanning Kelvin probe microscopy.[12] It should be noted that there is not a convinced evidence to prove that the observed potential barrier is due to the grain boundary. In another work,[13] however, the same author shows the presence of *intragrain* interfaces in CCTO grain. In fact, even if Chung would rather believe the grain boundary model, his work also suggests the possible presence of intragrain insulating barrier effects in CCTO grain.

In our recent work,[1] we identified the conduction paths in CCTO polycrystals by using AFM combined with SEM. We observed a *percolative conductive network* with a width of ~100 nm from the current mapping mode of AFM. In principle, such a percolative conduction network is unexpected for a polycrystalline sample with insulating grain boundaries surrounding semiconducting grains when the sample thickness is greatly larger than the grain size (our samples have thickness of ~150 μm and grain size of 2−10 μm), because the insulating grain boundaries should completely block all the conducting paths within the grains. By comparing the *percolative conduction network* to the network of grain boundaries obtained by SEM, we found that they are essentially similar from either the shape or the size and therefore concluded that the *percolative conduction network* is originated from the grain boundaries and the grain boundaries are conducting. We further show that the *electrically inhomogeneous structure* consisting of semiconducting and insulating regions is indeed present *within CCTO grains* and provides the main source of barriers between conductive and insulating regions. Our findings are completely opposite to what was expected so far for many authors like Chung but reasonably explain the phenomena observed in both polycrystals and single crystals.

First Chung claims that "thick grain boundaries of several tens of nanometers in width are, on a physical basis, unreasonable" because "The width of the grain boundaries in polycrystalline oxides including a variety of perovskite-type titanates is known to be in a range of a few nanometers". This comment is arbitrary. Even if this is true for many titanates, this does not mean that it is also true for CCTO. Actually, because there is not a *strict* definition on the width of grain boundary, for example, when the grain size is in a scale of a few nanometers, how can this author define the grain boundary? It should also be noted the difference between the grain-boundary within one grain and the interface between the adjacent two grains. Figure 1 given in Chung's comments shows that the interface between the

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(1) Fu, D.; Taniguchi, H.; Taniyama, T.; Itoh, M.; Koshihara, S.-Y. *Chem. Mater.* **2008**, *20*, 1694.
(2) Subramanian, M. A.; Li, D.; Duan, N.; Reisner, B. A.; Sleight, A. W. *J. Solid State Chem.* **2000**, *151*, 323–325.
(3) Adams, T. B.; Sinclair, D. C.; West, A. R. *Adv. Mater.* **2002**, *14*, 1312–1323.
(4) Homes, C. C.; Vogt, T.; Shapiro, S. M.; Wakimoto, S.; Ramirez, A. P. *Science* **2001**, *293*, 673–676.
(5) Moussa, S. M.; Kennedy, B. *J. Mater. Res. Bull.* **2001**, *36*, 2525–2529.
(6) He, L.; Neaton, J. B.; Cohen, M. H.; Vanderbilt, D. *Phys. Rev. B* **2002**, *65*, 214112.
(7) Maxwell, J. C. *Electricity and Magnetism*; Oxford University Press: Oxford, England, 1873; Vol. I, Sect. 328.
(8) Wagner, K. W. *Ann. Phys. (Leipzig)* **1913**, *40*, 53.
(9) Kalinin, S. V.; Shin, J.; Veith, G. M.; Baddorf, A. P.; Lobanov, M. V.; Runge, H.; Greenblatt, M. *Appl. Phys. Lett.* **2005**, *86*, 102902.
(10) Li, J.; Subramanian, M. A.; Rosenfeld, H. D.; Jones, C. Y.; Toby, B. H.; Sleight, A. W. *Chem. Mater.* **2004**, *16*, 5223–5225.
(11) Cohen, M. H.; Neaton, J. B.; He, L.; Vanderbilt, D. *J. Appl. Phys.* **2003**, *94*, 3299–3306.
(12) Chung, S.-Y.; Choi, S.-Y.; Yamamoto, T.; Ikuhara, Y.; Kang, S.-J. L. *Appl. Phys. Lett.* **2005**, *88*, 091917.
(13) Chung, S. Y. *Appl. Phys. Lett.* **2005**, *87*, 052901.

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adjacent two grains is extremely narrow, and unfortunately it does not tell us the thickness of the grain boundary of each grain to have an influence on their physical properties. When comparing the width of ~100 nm of the conductive layer to the grain size of ~2 μm to ~10 μm of our samples, our attribution of the conductive layer to the grain boundary is not physically unreasonable as claimed by Chung. In addition, it should be noted that the current mapping mode is a stand mode in most of commercially available AFM; there is no special difficulty to obtain the current images with a lateral resolution of ~10 nm as claimed by Chung.

In the second remark, Chung claims that Sample B, which underwent a thermal treatment by infrared radiation in an image furnace for increasing the grain size, "is not in a thermodynamically equilibrium state"; therefore, the results obtained by this sample are not reliable. This comment is also arbitrary. In fact, such infrared radiation is a standard technique to obtain the large crystals that have been used to demonstrate the giant dielectric response of CCTO single crystal in Homes et al.'s paper published in *Science*.[4] Our sample B does not show any essential differences from other CCTO samples without such thermal treatment from the X-ray diffraction and electrical measurements. As discussed in our paper,[1] we really observed that increasing the grain size leads to the higher current density. This observation is essentially in agreement with the TEM observation by Wu et al.,[14] which also showed that there is a higher density of the dislocations and planar defects in samples with larger grain size. However, one cannot ambiguously make a claim that a sample is under a thermodynamically equilibrium state merely due to its large defect density.

Chung's third remark is completely derived from his misunderstanding on our paper. In our paper,[1] on the basis of a simple double-layer model of the Maxwell−Wagner effect, we derived the following formula to explain the giant dielectric response in a system with heterostructural texture that has a conductive layer and an insulating layer

$$\varepsilon^* = (\varepsilon_1/a) + (\varepsilon_2/a\delta)(1/(1 + i\omega\tau)), \quad a = 1 + \delta\varepsilon_1/\varepsilon_2$$

where ε_1 and ε_2 are the dielectric constants of the conductive and insulating layers respectively, and δ is the volume fraction of the insulating regions. Given that $\varepsilon_1 = \varepsilon_2 \sim 100$ for CCTO, we explain that a volume fraction of insulating regions with $\delta = 0.001$ should lead to a giant value of 10^5 of dielectric constant for frequency $\omega = 0$. For our samples, we have given the values of $\varepsilon_1/a = 67$ and 96 and $\varepsilon_1/a\delta = 1008$ and 2716 for samples A and B, respectively, in Table 1 of our paper. Using these values, we can estimate $\delta = 6.6\%$ and 3.5% for samples A and B, respectively. These values are not incomparable to the observed current images when considering the fact that the density of the conducting path will increase greatly with the increase of the imaging voltage as shown in Figure 2 of our paper.[1]

As mentioned above and described in our paper,[1] the main source of barrier layers in CCTO is not provided by the conductive grain boundaries but is determined by the density of intragrain boundaries; we therefore make a remark that an effective way to control the electrical properties of CCTO is to control the defect density within a grain rather than the grain boundary. This remark is natural and reasonable.

As agreed by Chung in his final comment, "it is likely that nanoscale regions with different conductances are present within the CCTO crystals". In fact, some hint that these behaviors were already present in previous reports. Our contributions are that we unambiguously demonstrated such behavior by using a local probing technique of AFM combined with SEM and successfully modeled the temperature and frequency dependences of dielectric response in CCTO. Anyway, we believe the readers of *Chemistry of Materials* and related fields will make a correct judgment on our paper.

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(14) Wu, L.; Zhu, Y.; Park, S.; Shapiro, S.; Shirane, G. *Phys. Rev. B* **2005**, *71*, 014118.