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Grain Growth-Controlled Giant Permittivity in Soft Chemistry CaCu$_3$Ti$_4$O$_{12}$ Ceramics

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We report a dielectric constant of up to 5.4×10^5 at room temperature and 1 kHz for CaCu$_3$Ti$_4$O$_{12}$ (CCTO) ceramics, derived from multiphase powders (coprecipitation products), made by a "chimie douce" (coprecipitation) method, and then sintered in air. The sintered products are pure-phase CCTO ceramics. The high dielectric constant is achieved by tuning the size of grains and the thickness of grain boundaries. The grain growth is controlled by varying the concentration of excess CuO in the initial powder (calcined coprecipitation products) between 1 and 3.1 wt%. The dielectric constant of pure CCTO ceramics increases with the initial CuO concentration, reaching its maximum at 2.4 wt% of CuO. A further increase of excess CuO in powders results in a permittivity decrease, accompanied by the formation of CuO as a separate phase in the sintered products. The unusual grain growth behavior is attributed to a eutectic reaction between CuO and TiO$_2$ present in the initial powder.

I. Introduction

A CONTINUING drive toward further miniaturization in microelectronics stimulates the search for new high-permittivity materials, whose performance in devices such as capacitors is not compromised as the size of components becomes smaller. Since the discovery of high permittivity ($\sim 1.2 \times 10^4$ at 1 kHz) in CaCu$_3$Ti$_4$O$_{12}$ (CCTO) by Subramanian et al., in 2000,[1] CCTO has become a promising candidate to replace commonly used high-dielectric materials. The origins of this extraordinary high permittivity are not clear and are intensively discussed in the literature.[2–8] To explain the temperature behavior of permittivity in CCTO single crystals, Homes et al.[2] and Ramirez et al.[9] suggested a polarization mechanism involving displacement of Ti^{4+} ions from the center of symmetry within the octahedral sites, for which there has been no experimental evidence so far. Li et al.[10] and Whangbo and Subramanian[11] argue that intrinsic twin boundaries or planar defects are responsible for the high permittivity in CCTO. Fang and Liu[12] conducted a detailed scanning electron microscopy (SEM) and high-resolution transmission electronic microscopy (HRTEM) study and found insulating domains inside the grains as possible sources of the huge dielectric response in both single-crystal and polycrystalline CCTO samples.

After the work of Sinclair et al.,[13] the one-step internal barrier layer capacitor (IBLC) model is widely accepted as a useful tool to analyze the dielectric properties of CCTO.[14–17] This model utilizes two variables, the average grain size of semiconducting grains A and the average thickness of grain boundaries t, to estimate the effective permittivity of a given material from the dielectric constant of the insulating layers ε_{GB}[18]:

$$\varepsilon_{eff} \approx \varepsilon_{GB} \frac{A}{t} \qquad (1)$$

Equation (1) provides general guidance in interpreting the dielectric responses of systems consisting of semiconducting grains and insulating boundaries, but care should be exercised, as it cannot be used straightforwardly to describe the giant permittivity in single-crystal and multicomponent CCTO samples.[19] We utilize the IBLC model to calculate the thickness of grain boundaries from the dielectric constants of grain boundaries and grain size. The experimental proof of the IBLC model is not the purpose of the study.

According to Eq. (1), if one can achieve a high A/t ratio by tuning the size of grains and the thickness of grain boundaries, a material with an extremely high effective permittivity can be obtained. However, the grain growth mechanism involved in the sintering process and the factors affecting the high dielectric response are still unclear. Among other factors, the chemistry of grain boundaries, time, temperature, and atmospheric conditions during sintering should be taken into account. For example, Fang and colleagues[7,20] pointed to the Cu segregation in the grain boundaries as a plausible mechanism for creating insulating layers. Bender and Pan[21] reported a high permittivity in CCTO ceramics obtained by a multistep annealing procedure in Ar. They attributed the effect of the Ar atmosphere to the formation of oxygen vacancies.

The synthesis of CCTO described in this study is a two-stage process. In contrast to the majority of papers on CCTO,[1–21] we use a soft synthesis method to obtain initial powders using oxalate precursors. The final products of the first step are calcined samples. These samples are not used in dielectric constant measurements. The powder samples are then sintered in air to transform powder samples into single-phase CCTO ceramics. We vary the excess concentration of CuO present as a minor phase in the initial CCTO powder samples (calcined coprecipitation products). Other conditions, such as sintering

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time and temperature, are kept constant. Therefore, grain growth is a dominant factor in determining changes in the dielectric responses of CCTO ceramics. The soft chemistry method used in the study has been described before, but the effects of the initial powder composition on phase purity grain growth and dielectric response have not been reported.

The main focus of this study is on relationships between the composition/structure of the initial powders and the structure/dielectric properties of the sintered products. By adjusting the composition of the initial powders, we can control the dielectric properties of the final sintered samples prepared under the same temperature/time/atmosphere conditions. We find that the excess CuO content in the initial powder correlates with the A/t ratio, and thus the dielectric constant (Eq. (1)). An increase in the CuO content results in an increase in the A/t ratio, as long as the final product appears to be single phase. We attribute the role of excess CuO in dielectric responses of CCTO to the formation of a eutectic between CuO and TiO_2, which facilitates grain growth during sintering.

A permittivity of $\sim 5.40 \times 10^4$ at 1 kHz (double the previously reported value obtained for ceramics sintered in the air atmosphere) has been achieved. Currently, the highest dielectric value reported is $\sim 3.0 \times 10^5$ for ceramics from powder samples prepared by ball milling and sintered at 1000°C for 24 h with a minimum dielectric loss of about 0.1 at 2 kHz.[3]

II. Experimental Procedure

Samples with various CuO contents (abbreviated as CCTO-01, CCTO-02, CCTO-03, CCTO-04, and CCTO-05, indicating the increasing amount of CuO as a separate phase imbedded in pure CCTO) were obtained by a coprecipitation method and calcinated in air. This process allows one to tune the chemistry of the oxalate precursors and, hence, the chemical composition of the calcined coprecipitation products (CuO to a pure-phase CCTO ratio). The precursors were derived at room temperature from metal chlorides ($CaCl_2$, $CuCl_2 2H_2O$, and $TiCl_3$) and oxalic acid in water and ethanol media (H_2O:EtOH 1:5), respectively.[22] The initial amounts of metal cations were varied in such a way that the Ca/Ti ratio remained stoichiometric (1:4), while the quantity of copper chloride was varied to achieve the desired CuO proportion in the powder. The precipitates, centrifuged and dried at 100°C overnight, were then calcined in air at 950°C for 10 h to obtain the initial powder. Then, the calcined powder, mixed with an organic binder (polyvinyl alcohol), was uniaxially pressed into pellets (6 mm × 1.2 mm). Finally, the pellets were sintered at 1100°C for 24 h in static air. The density of the pellets was measured by the Archimedes method.

The morphology and grain size of the powders and ceramics were analyzed by SEM using a JEOL 6400F microscope (Tokyo, Japan) equipped with a Links energy-dispersive X-ray spectroscopy (EDS) detector and by a field emission gun (FEG-SEM) utilizing a JEOL JSM 6700 instrument. The granulometric analysis of digitized SEM images was performed using public domain software "IMAGEJ."[23] The crystal structure of CCTO and minor phases (CuO, TiO_2, and $CaTiO_3$) were confirmed by powder X-ray diffraction (XRD) carried out on a Seiffert 3003 TT (Bergisch Gladbach, Germany) using $CuK\alpha$ radiation (40 kV and 40 mA) in a 2θ range 15°–120° with a step of 0.02° and a dwell time of 10 s. The Rietveld method was used to analyze the phases in the powder samples (to calculate the excess CuO concentration) quantitatively utilizing the FULL-PROF program.[24]

To achieve good conduction, both sides of the disk-shaped pellets were covered with silver paint and fired at 700°C for 20 min. The relative permittivity measurements were conducted on an HP 4194A apparatus (Yokogama-Hewlett-Packard Ltd., Tokyo, Japan) in the range 100 Hz–1 MHz under a voltage amplitude of 1 V. All measurements were carried out at ambient temperature. The error of the effective permittivity measurements was estimated to be 5%.
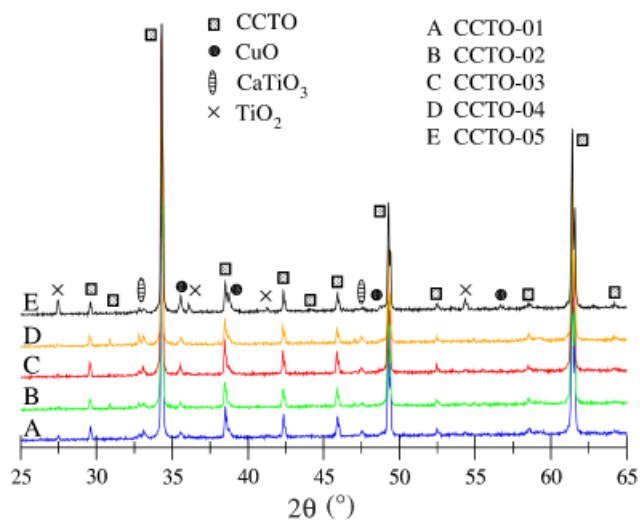

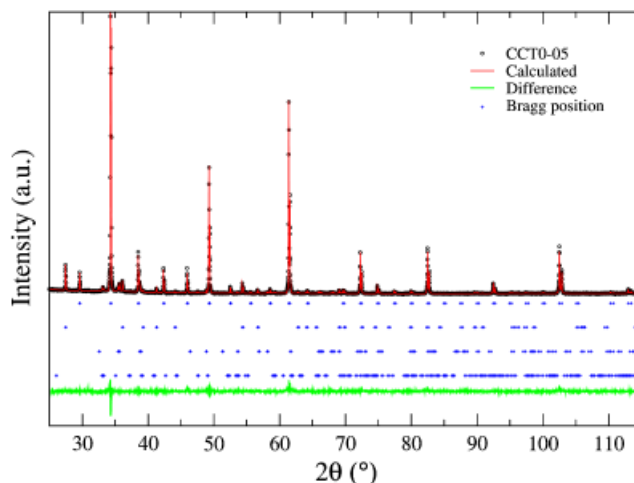**Fig. 1.** X-ray diffraction patterns of various $CaCu_3Ti_4O_{12}$ multiphase powder samples obtained at 950°C for 10 h.

Fig. 2. Rietveld analysis for $CaCu_3Ti_4O_{12}$-05 (dots indicate the experimental data, the solid line indicates the calculated pattern, and the difference between experimental and calculated graphs is shown at the bottom). The Bragg peaks for observed phases are shown as stars. $R_p = 0.204$, $R_{wp} = 0.148$, $R_{exp} = 0.086$, $\chi^2 = 2.947$.
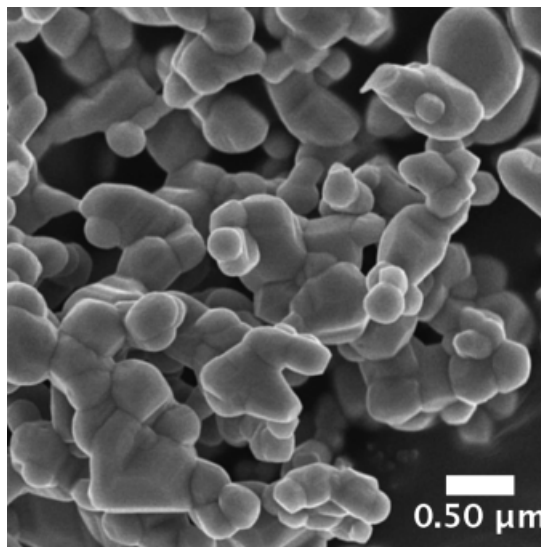

Fig. 3. Typical field emission gun-scanning electron microscopy micrograph of the $CaCu_3Ti_4O_{12}$ (CCTO)-based powder (CCTO-03) calcined at 950°C for 10 h.

III. Results and Discussion

As indicated above, the synthesis of CCTO is a two-stage process. The final products of the first step were calcined samples, whose X-ray patterns are shown in Fig. 1. These samples were not used in the dielectric constant measurements. In addition to a dominant pure CCTO phase, the results indicate the presence of small amounts of CuO, $CaTiO_3$, and TiO_2 phases in the powders calcined at 950°C for 10 h.

Figure 2 gives a typical refinement pattern (CCTO-05 in this case). The amount of CuO, as supported by XRD, is controlled by the amount of metal chlorides used in the mixture at the coprecipitation stage. The X-ray analyses for sintered CCTO-01, CCTO-02, and CCTO-03 ceramics (not shown) conform to a single-phase CCTO structure, while other samples have traces of CuO.

The FEG-SEM micrographs of CCTO (Fig. 3) show clumps of submeter sized grains, typical for powder samples calcined at 950°C. The grains are homogeneous in terms of shape and size.

The SEM images of the CCTO ceramics sintered at 1100°C for 24 h, presented in Fig. 4, indicate the growth of grains and grain boundaries as a function of CuO content in the initial powder CCTO samples. The EDS (not shown) and XRD analyses confirm that the phase, seen as white grain boundaries in chemical contrast SEM images for CCTO-04 and 05, is excess CuO, implying that the CuO phase grows by segregation in the grain boundaries.

Here, we probe the correlations between excess CuO content in powders, and the size of grains and grain boundaries in sintered samples using a granulometric method (statistical analysis of particle size distribution) for 70–390 particles in SEM images (from 390 particles for CCTO-01 to 70 particles for CCTO-05).

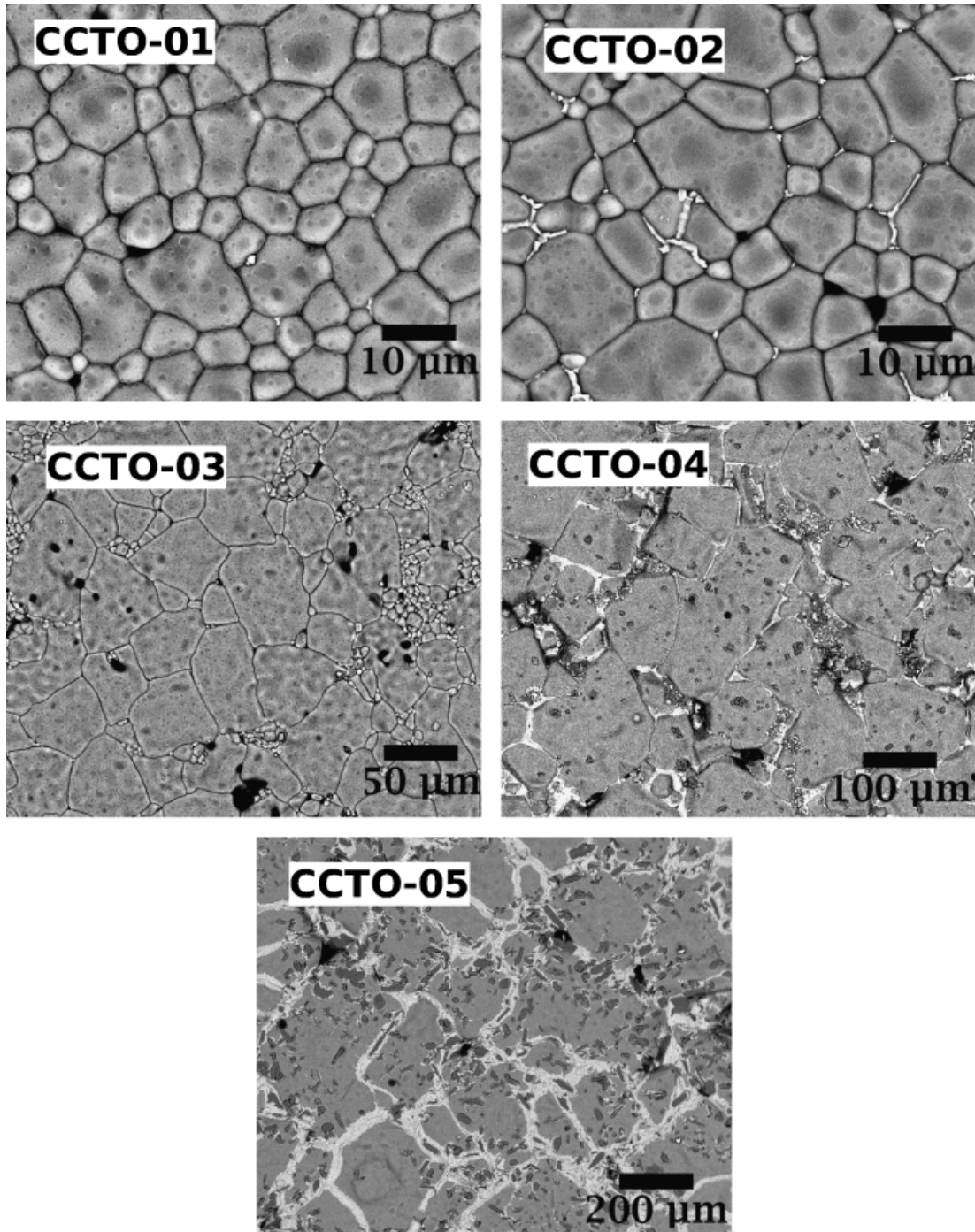**Fig. 4.** Chemical contrast scanning electron microscopy micrographs of $CaCu_3Ti_4O_{12}$ (CCTO) ceramics. The increasing number in the abbreviation (CCTO-01, 02, 03, 04, and 05) corresponds to the increase of CuO content in the powder used to form the ceramics.
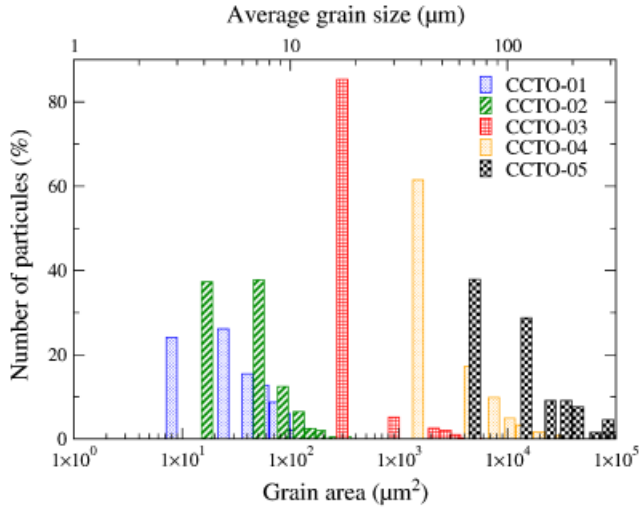
Fig. 5. Granulometry of binary scanning electron microscopy images: grain area and size distribution for all CaCu₃Ti₄O₁₂ samples.

Fig. 5. Granulometry of binary scanning electron microscopy images: grain area and size distribution for all $CaCu_3Ti_4O_{12}$ samples.

Table I. CCTO Characteristics: Eq. (1) Parameters, CuO wt%, and Density of the CCTO Samples

Sample	Density (g/cm³)	CuO concentration (wt%)	ε_{eff}	Grain size A (µm)	Thickness t, (nm) (calculated from Eq.(1))	A/t ratio
CCTO-01	4.73	0.93 (6)	16 600	6.0	72	83
CCTO-02	4.88	2.00 (7)	258 000	8.0	6	1290
CCTO-03	4.76	2.39 (9)	539 000	22.9	8	2695
CCTO-04	4.87	2.87 (7)	177 000	64.5	—	—
CCTO-05	4.79	3.12 (8)	47 000	141.7	—	—

pure CCTO,[1–7] the dielectric responses essentially remain constant over the wide frequency range from 100 to $\sim 10^5$ Hz for all samples. But for the CCTO-03 sample with the highest dielectric permittivity value, the dielectric response rapidly decreases above 2×10^4 Hz.

The dielectric constant values at 1 kHz for all CCTO samples are given in Table I. The permittivity of sintered samples reaches a maximum of 539 000 and then decreases with increasing CuO content in the powders before sintering. The CCTO-03 sample with the highest dielectric constant value has a narrow grain size distribution compared with the other four samples (Fig. 5). The average grain size for CCTO-03 is relatively large (~ 23 µm).

Here, we utilize the IBLC model (Eq. (1)) to calculate the thickness of grain boundaries from the effective permittivity ε_{eff} measured at 1 kHz, the relative permittivity of the insulating grain boundaries ε, and the average grain size A and the average thickness t of grain boundaries. The values for all terms in Eq. (1), along with the densities of the pellets, are reported in Table I. The high densities measured can be explained by the formation of a liquid CuO–TiO₂ phase during the sintering process, because the liquid phase can assist the densification of the ceramics. Pan and Bender[27] assumed the dielectric constant of the insulating grain boundary to be 200 for the CCTO ceramics. The calculated thickness is in nanometer range as suggested by Calvert et al.[28] and is consistent with our HRTEM results, which will be published elsewhere. Comparison between the calculated and observed values of the grain boundary thickness suggests that the IBLC model reflects the dominant factors controlling the dielectric responses of CCTO. We cannot exclude other factors such as the chemistry of grain boundaries or crystal defects that may be present in crystals and influence the calculation of thickness of grain boundaries using the IBLC model.

As the Cu content increases further, the permittivity decreases, consistent with the formation of a separate CuO phase detected by SEM (see discussion above), which hampers the dielectric response of the material. Moreover, for two samples (CCTO-04 and 05), the presence of a CuO phase in grain boundaries makes it impossible to apply the simple Eq. (1). ε_{eff} values are plotted in Fig. 7 as a function of the average grain size (Fig. 7(a)) and the CuO content in the CCTO powders (Fig. 7(b)). Mauckzok and Wernicke[18] and Aygün et al.[29] studied the effects of excess CuO on the dielectric properties of CCTO. The work of Aygün et al.[29] considered a model that included the CuO phase surrounding the grains of pure CCTO. These studies showed a decrease of permittivity with increasing CuO content. Our study confirms their findings. Samples CCTO-4 and -5 have CuO as a minor phase even after sintering and show a diminishing permittivity with increasing CuO content.

The highest permittivity of 539 000 was obtained for the maximum A/t ratio of 2695 in the single-phase CCTO from the initial powder with 2.4 wt% CuO, above which the ceramics become multiphase. Detailed TEM, to determine the microstructure of grains and grain boundaries, as well as impedance spectroscopy studies are in progress. It is also important to investigate the sintering conditions of multiphase CCTO such as sintering time and atmosphere as the final permittivity is directly related to the microstructure.

The grain size of CTTO samples with varying initial CuO content lies between 6 and 140 µm.

Figure 5 shows the distributions of grain areas for all five samples. The results confirm that increasing the CuO content in the powders correlates with the grain growth. The grain growth observed may be explained by the formation of a CuO–TiO₂ eutectic rich in CuO during the sintering process. The CuO–TiO₂ eutectic has been found by Lu et al.[25] at a temperature as low as 919°C. Note, calcination and sintering of CCTO are performed at different temperatures (950° and 1100°C, respectively). We believe that a liquid phase of a CuO–TiO₂ eutectic at sintering temperature is responsible for the observed grain growth mechanism, that is, the grain size appears to be dependent on the amount of minor phases (CuO, TiO₂, etc.) in the initial powders under the same time/temperature conditions. We used the content of the major impurity phase, namely, CuO, in the initial powders as a measure of the eutectic concentration, because the real amount of liquid phase is hard to determine (the maximum CuO content studied in the initial powder is 3.1%). The amount of liquid phase apparently controls the crystal growth at grain boundaries, resulting in large grains while keeping the grain boundaries thin. A similar phenomenon was observed by Yang[26] in $(Ba_{1-x}Sr_x)(Ti_{0.9}Zr_{0.1})O_3$ compounds.

Now, we examine the frequency dependencies of the dielectric constant and dielectric loss for sintered CCTO samples. The results are shown in Fig. 6. In agreement with previous studies on
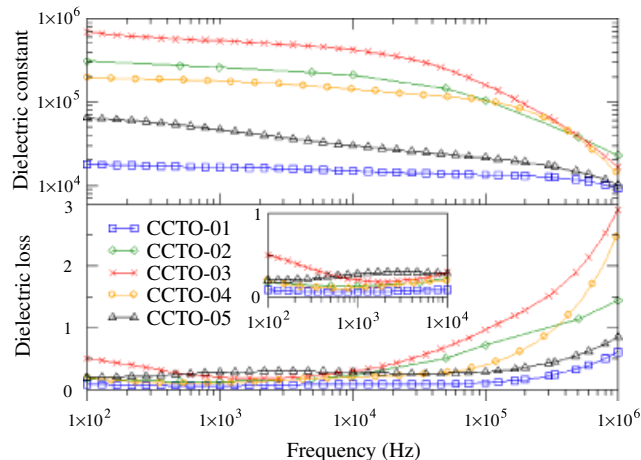

Fig. 6. Frequency dependencies of dielectric constant and dielectric loss for the CaCu₃Ti₄O₁₂ samples measured at ambient temperature.

Fig. 6. Frequency dependencies of dielectric constant and dielectric loss for the $CaCu_3Ti_4O_{12}$ samples measured at ambient temperature.
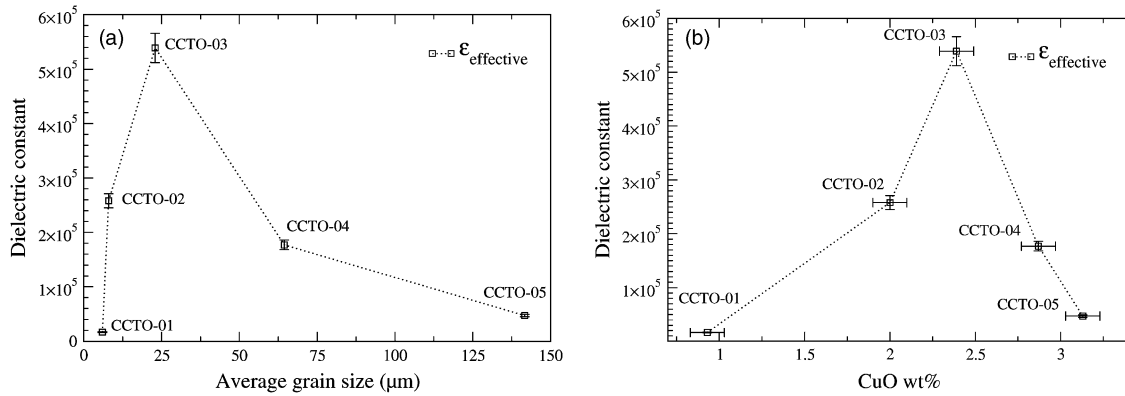
Fig. 7. Effective permittivity (measured at 1 kHz) plotted as a function of (a) the average grain size and (b) the CuO wt%.

IV. Conclusions

Thus, we link the CuO content in the powder samples (calcined coprecipitation products before sintering in air) to the grain growth in the ceramics studied. The grain growth in CCTO ceramics is delicately controlled by small amounts of excess CuO, which forms a eutectic with TiO_2 in the initial powders at the sintering temperature. We have been able to obtain huge dielectric constant CCTO ceramics by varying the concentration of CuO in the coprecipitation products. A permittivity of 539 000 (approximately twice the value reported previously) and low dielectric loss (0.2) were obtained without annealing by increasing the A/t ratio up to 2695 in the single-phase CCTO ceramics. More information on the chemistry and microstructure of the grain boundary regions is required to better understand the observed phenomena.

References

[1]M. A. Subramanian, D. Li, N. Duan, B. A. Reisner, and A. W. Sleight, "High Dielectric Constant in $ACu_3Ti_4O_{12}$ and $ACu_3Fe_4O_{12}$ Phases," *J. Solid State Chem.*, **151**, 323–5 (2000).

[2]C. C. Homes, T. Vogt, S. M. Shapiro, S. Wakimoto, and A. P. Ramirez, "Optical Response of High-Dielectric-Constant Perovskite-Related Oxide," *Science*, **293**, 673–6 (2001).

[3]T. B. Adams, D. C. Sinclair, and A. R. West, "Giant Barrier Layer Capacitance Effects in $CaCu_3Ti_4O_{12}$ Ceramics," *Adv. Mater.*, **14**, 1321–3 (2002).

[4]A. R. West, T. B. Adams, F. D. Morrison, and D. C. Sinclair, "Novel High Capacitance Materials: $BaTiO_3$:La and $CaCu_3Ti_4O_{12}$," *J. Eur. Ceram. Soc.*, **24**, 1439–48 (2004).

[5]C. C. Homes, T. Vogt, S. M. Shapiro, S. Wakimoto, M. A. Subramanian, and A. P. Ramirez, "Charge Transfer in the High Dielectric Constant Materials $CaCu_3Ti_4O_{12}$ and $CdCu_3Ti_4O_{12}$," *Phys. Rev. B.*, **67**, 092106 (2003).

[6]P. Lunkenheimer, R. Fichtl, S. G. Ebbinghaus, and A. Loidl, "Nonintrinsic Origin of the Colossal Dielectric Constants in $CaCu_3Ti_4O_{12}$," *Phys. Rev. B.*, **70**, 172102 (2004).

[7]T.-T. Fang and H.-K. Shiau, "Mechanism for Developing the Boundary Barrier Layers of $CaCu_3Ti_4O_{12}$," *J. Am. Ceram. Soc.*, **87**, 2072–9 (2004).

[8]L. Zhang, "Electrode and Grain-Boundary Effects on the Conductivity of $CaCu_3Ti_4O_{12}$," *Appl. Phys. Lett.*, **87**, 022907 (2005).

[9]A. P. Ramirez, M. A. Subramanian, M. Gardel, G. Blumberg, D. Li, T. Vogt, and S. M. Shapiro, "Giant Dielectric Constant Response in a Copper-Titanate," *Solid State Commun.*, **115**, 217–20 (2000).

[10]J. Li, A. W. Sleight, and M. A. Subramanian, "Evidence for Internal Resistive Barriers in a Crystal of the Giant Dielectric Constant Material: $CaCu_3Ti_4O_{12}$," *Solid State Commun.*, **135**, 260–2 (2005).

[11]M.-H. Whangbo and M. A. Subramanian, "Structural Model of Planar Defects in $CaCu_3Ti_4O_{12}$ Exhibiting a Giant Dielectric Constant," *Chem. Mater.*, **18**, 3257–60 (2006).

[12]T.-T. Fang and C. P. Liu, "Evidence of the Internal Domains for Inducing The Anomalously High Dielectric Constant of $CaCu_3Ti_4O_{12}$," *Chem. Mater.*, **17**, 5167–71 (2005).

[13]D. C. Sinclair, T. B. Adams, F. D. Morrison, and A. R. West, "$CaCu_3Ti_4O_{12}$: One-Step Internal Barrier Layer Capacitor," *Appl. Phys. Lett.*, **80**, 2153–5 (2002).

[14]S.-Y. Chung, I.-D. Kim, and S.-J. L. Kang, "Strong Nonlinear Current–Voltage Behavior in Perovskite-Derivative Calcium Copper Titanate," *Nat. Mater.*, **3**, 774–8 (2004).

[15]S.-Y. Chung, S.-Y. Choi, T. Yamamoto, Y. Ikuhara, and S.-J. L. Kang, "Site-Selectivity of 3d Metal Cation Dopants and Dielectric Response in Calcium Copper Titanate," *Appl. Phys. Lett.*, **88**, 091917 (2006).

[16]R. K. Grubbs, E. L. Venturini, P. G. Clem, J. J. Richardson, B. A. Tuttle, and G. A. Samara, "Dielectric and Magnetic Properties of Fe- and Nb-doped $CaCu_3Ti_4O_{12}$," *Phys. Rev. B.*, **72**, 104111 (2005).

[17]T. B. Adams, D. C. Sinclair, and A. R. West, "Characterization of Grain Boundary Impedances in Fine- and Coarse-Grained $CaCu_3Ti_4O_{12}$ Ceramics," *Phys. Rev. B.*, **73**, 094124 (2006).

[18]R. Mauczok and R. Wernicke, "Ceramic Boundary-Layer Capacitors," *Philips Tech. Rev.*, **41**, 338–47 (1983).

[19]M. H. Cohen, J. B. Neaton, L. He, and D. Vanderbilt, "Extrinsic Models for the Dielectric Response of $CaCu_3Ti_4O_{12}$," *J. Appl. Phys.*, **94**, 3299–306 (2003).

[20]T.-T. Fang, L.-T. Mei, and H.-F. Ho, "Effects of Cu Stoichiometry on the Microstructure, Barrier-Layer Structures, Electrical Conduction, Dielectric Responses, and Stability of $CaCu_3Ti_4O_{12}$," *Acta. Mater.*, **54**, 2867 (2006).

[21]B. A. Bender and M.-J. Pan, "The Effect of Processing on the Giant Dielectric Properties of $CaCu_3Ti_4O_{12}$," *Mater. Sci. Eng. B*, **117**, 339 (2005).

[22]L. Marchin, S. Guillemet-Fritsch, and B. Durand, "Soft Chemistry Synthesis of the Perovskite $CaCu_3Ti_4O_{12}$," *Prog. Solid State Chem.*, **38**, 151–5.

[23]W. S. Rasband and J. Image. US National Institutes of Health, Bethesda, MD, http://rsb.info.nih.gov/ij/(1997–2006).

[24]Program Fullprof 2k, Version 2.60-Mars 2004-LLB JRC.

[25]F.-H. Lu, F.-X. Fang, and Y.-S. Chen, "Eutectic Reaction between Copper Oxide and Titanium Dioxide," *J. Eur. Ceram. Soc.*, **21**, 1093–9 (2001).

[26]YC. F. Yang, "Improvement of the Sintering and Dielectric Characteristics of Surface Barrier Layer Capacitors by CuO Addition," *Jpn. J. Appl. Phys.*, **35**, 1806–13 (1996).

[27]M-J. Pan and B. A. Bender, "A Bimodal Grain Size Model for Predicting the Dielectric Constant of Calcium Copper Titanate Ceramics," *J. Am. Ceram. Soc.*, **88**, 2611–4 (2005).

[28]C. C. Calvert, W. M. Rainforth, D. C. Sinclair, and A. R. West, "Characterisation of Grain Boundaries in $CaCu_3Ti_4O_{12}$ using HREM, EDS and EELS," *J. Phys: Conf. Ser.*, **26**, 65–8 (2006).

[29]S. Aygün, X. Tan, J.-P. Maria, and D. Cann, "Effects of Processing Conditions on the Dielectric Properties of $CaCu_3Ti_4O_{12}$," *J. Electroceram.*, **15** [3] 203–8. □