PHYSICAL REVIEW B **74**, 024106 (2006)

Oxygen-vacancy-related dielectric anomaly in $CaCu_3Ti_4O_{12}$: Post-sintering annealing studies

C. C. Wang and L. W. Zhang*
Physics Department, Laboratory of Advanced Materials, Tsinghua University, Beijing 100084, People's Republic of China

(Received 8 December 2005; revised manuscript received 8 June 2006; published 14 July 2006)

The influence of post-sintering annealing on the dielectric properties of $CaCu_3Ti_4O_{12}$ was investigated in the temperature range form 200 to 400 K. A dielectric peak featuring thermally activated Debye-like behavior was observed around 340 K (100 Hz). This peak can be eliminated by annealing in oxidizing atmosphere and created by annealing in reducing atmosphere. The dielectric peak was explained in terms of the combinational contributions from the *n*- and *p*-type carriers.

DOI: 10.1103/PhysRevB.74.024106 PACS number(s): 77.22.Ch, 77.84.Dy

Titanates with perovskite-type structure have been attracting much attention for a long time because of their versatile dielectric, ferroelectric, and even superconducting properties, which can be easily tuned by chemical doping as well as changing in oxygen content. For instance, with increasing the concentration of oxygen vacancy, $SrTiO_3$ can change from a semiconductor to a metal, which becomes a superconductor at low enough temperatures.[1] Recently, a newly discovered ATiO$_3$-tpye perovskite titanate $CaCu_3Ti_4O_{12}$ [$Ca_{1/4}Cu_{3/4}TiO_3$ (CCTO)] was extensively investigated due to its giant dielectric constant ($\varepsilon' \sim 10^4-10^5$) and weak temperature dependence in a wide temperature range from 100 to 600 K,[2–4] whose underlying mechanism is not well settled. The giant dielectric response of this titanate was found to be very sensitive to the processing conditions.[5] The different electric transport behavior within a grain and across a boundary of a CCTO ceramic was proposed to result from the different oxygen content between the grain and the boundary.[6] Our preliminary study[7] also showed that annealing treatments in reducing (nitrogen) and oxidizing (oxygen) atmospheres would have drastic changes in dielectric properties near room temperatures. These results strongly suggest that the concentration of oxygen might play an important role in the dielectric properties of CCTO. So far, most attention has been paid to the drastic transition from the high dielectric constants to the low ones.[1–5] Although Chen[8] investigated the high temperature electrical properties of highly epitaxial CCTO thin films, few results are reported about the effects of oxygen concentration on the dielectric properties at temperatures higher than the room temperature at which most practical electronic devices are operated. Therefore, detailed investigations of the influence of oxygen vacancy on the dielectric behavior in a wider temperature range can not only deepen the understanding of the intriguing dielectric property of CCTO, but also be helpful to optimize the preparing conditions for future potential applications.

In the present work, the low frequency ($100\ \mathrm{Hz} \leqslant f \leqslant 100\ \mathrm{kHz}$) dielectric properties of CCTO samples after different annealings were studied. In addition to the previously reported surface layer effect at about 250 K, a new dielectric peak in ε' appears at about 340 K without being accompanied by a peak in the loss tangent. This dielectric anomaly was ascribed to the polarization from both the *n*- and *p*-type carriers.

Single phase CCTO pellets used for dielectric measurements were prepared by solid-state reaction. Details about the sample preparation were given elsewhere.[7] Temperature-dependent dielectric properties were measured using a QuadTech 1730 LCR Digibridge in a frequency range from 100 to 100 kHz with a cooling/heating rate of 2 K/min. Silver paste was used as the electrodes. In order to investigate the effects of the oxygen vacancy on the dielectric properties, the as-prepared sample was annealed in flowing (200 ml/min) oxygen and nitrogen (both with purity >99.999%). The post-annealing processes consists of several consecutive steps: (1) annealed in O_2 at 900 °C for 2 h, denoted as $A1$; (2) annealed in N_2 at 900 °C for 2 h after $A1$, denoted as $A2$; and (3) annealed in O_2 at 800 °C for 2 h after $A2$, denoted as $A3$.

Figure 1 displays the dielectric properties of a CCTO pel-

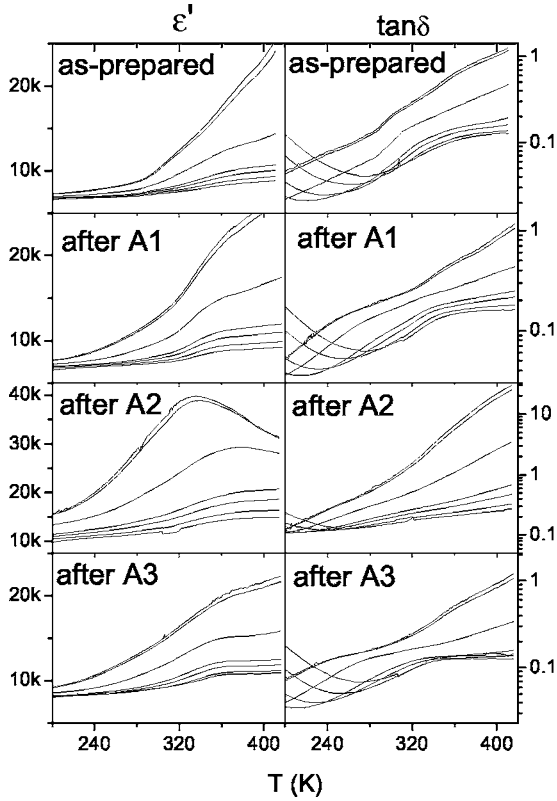

FIG. 1. Temperature dependence of ε' (left) and tan δ (right) for the CCTO sample before (as-prepared) and after several annealing processes at the measuring frequencies of 100, 120, 1000, 10 000, 20 000, 50 000, and 100 000 Hz (from top to bottom).

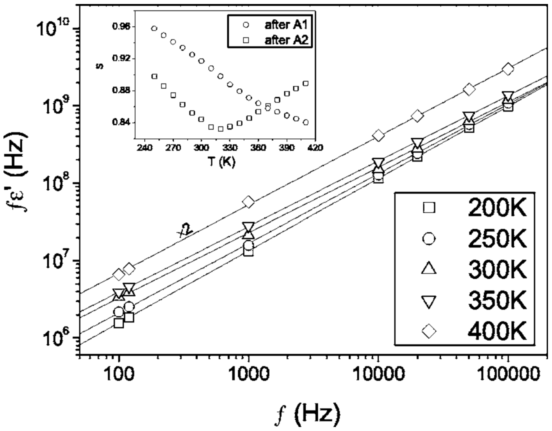

FIG. 2. Plot of $\log_{10}(f\varepsilon')$ against $\log_{10}f$ at several fixed temperatures for the CCTO sample after $A2$. To see clearly, the data point values for 400 K are scaled up by factor of 2. The solid lines are results of the best linear fittings based on Eq. (2). Inset shows the temperature dependence of s obtained from the fittings for the sample after $A1$ and $A2$.

let before (as-prepared) and after several annealing processes at a number of frequencies. For the as-prepared sample, the drastic increase in ε' at high temperatures is caused by conductivity as indicated later. The obvious upturn in tan δ at low temperatures for the curves of high frequencies is due to the relaxation widely studied before in CCTO. It is worth noting that the so-called 250 K peak[7] usually observed at about 250 K in tan δ ($\sim$100 Hz) is not clear in this as-prepared sample. After process $A1$, the dielectric behavior keeps almost unchanged except for the emergence of 250 K peak in tan δ pronounced in low frequencies. However, after process $A2$, notable changes can be seen: (1) both ε' and tan δ increase largely; (2) ε' registers a peak around 340 K (100 Hz); (3) the 250 K peak disappears and tan δ increases near-exponentially with increasing temperature without visible anomaly in the vicinity of 340 K, implying that the peak in ε' is not likely caused by the relaxation process. Upon increasing the measured frequency, the peak position of ε' was shifted to higher temperatures and the peak height decreased, which is typical of a thermally activated Debye-like behavior. Finally after step $A3$, both the magnitudes and the temperature dependence of ε' and tan δ are recovered to the case before $A2$, and the 250 K peak reappears. As proposed in our previous paper,[7] the 250 K peak arose from the surface layer effect due to the inhomogeneous distribution of oxygen vacancy. The fact that the dielectric peak around 340 K (hereafter referred to as 340 K peak) can be eliminated by annealing in oxidizing atmosphere and created by annealing in reducing atmosphere strongly suggest that the 340 K peak is closely related to oxygen vacancies which made the grains of the CCTO ceramic more conductive.[6] Therefore, the 340 K peak might be linked with the conductivity, and the dielectric behavior should follow the universal dielectric law (UDR).[9] According to this model, ε' can be calculated as

$$\varepsilon' = \tan(s\pi/2)\sigma_0 f^{s-1}/\varepsilon_0 \tag{1}$$

where σ_0 and frequency exponent s are temperature dependent, ε_0 the electric permittivity of free space. Equation (1) can be rewritten as

$$f\varepsilon' = A(T)f^{s}, \tag{2}$$

with the temperature-dependent constant $A(T) = \tan(s\pi/2)\sigma_0/\varepsilon_0$. Therefore, at a given temperature, a straight line with a slope of s should be obtained if $\log_{10}(f\varepsilon')$ is plotted as a function of $\log_{10} f$, which is evidenced in Fig. 2. The same behavior was also found in the as-prepared and O_2-annealed cases, which indicates that, just as recently reported in CCTO thin films,[10] the carrier polarization is responsible for the dielectric behavior of CCTO ceramic samples. The values of the parameter s deduced from linear fittings are presented in the inset of Fig. 2. A noteworthy feature is that in both N_2-annealed and O_2-annealed cases the deduced parameters s bear a linear relationship with the temperature, which has also been reported in $YBa_2Cu_3O_{6+x}$[11] and La_2CuO_{4+x} ceramics.[12] The distinct difference between the two cases is that for the N_2-annealed CCTO sample, with increasing temperature the slope of the linear temperature dependence changes from a negative to a positive value at the transition temperature $\sim$320 K. This change in slope might imply an alternation of the polarization mechanism.

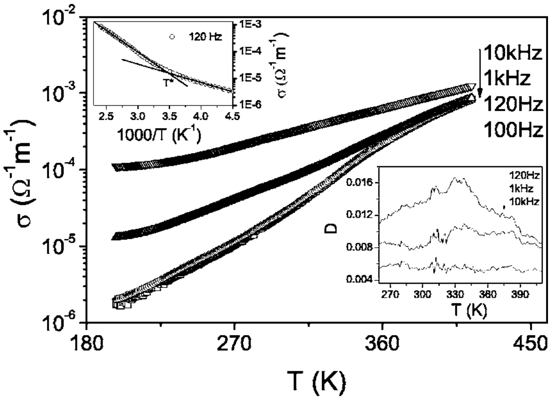

FIG. 3. Temperature dependence of ac conductivity σ at different frequencies for CCTO sample after the annealing treatment of $A2$. The upper inset shows the Arrhenius relation of σ vs $1/T$ for the data obtained at 120 Hz. The straight lines shown as a guide to the eye illustrate the thermally activated behavior at low and high temperature ranges with a crossover temperature of T^{*}. The lower inset presents the temperature dependent of the logarithmic derivative D (defined in the text) at various frequencies.

Figure 3 presents the ac conductivity (σ) of the same sample as in Fig. 1 after $A2$ process. Being consistent with the UDR law, the ac conductivity increases with measuring frequencies, especially at low temperatures. When the measuring frequency is lower than 120 Hz, the ac conductivity is almost independent on the measuring frequencies. Therefore, the ac conductivity at 120 Hz can be approximately treated as the dc conductivity. It is seen that there is a greater increase in σ at 120 Hz in the temperature range of the 340 K peak, which is clearly demonstrated from the temperature dependence of the logarithmic derivatives, D, defined as $D = \partial \log_{10} \sigma / \partial T$, as shown in the lower inset of Fig. 3. A well-defined peak at 330 K on the curve of 120 Hz indicates that another conduction mechanism may come into action. The Arrhenius plot, $\ln(\sigma)$ versus $1/T$, for the conductivity at 120 Hz (upper inset of Fig. 3) exhibits two linear regions at higher and lower temperatures, respectively, with the intersection temperature $T^{*} \approx 285$ K. The activation energy for the high temperature region is 0.33 eV and 97 meV for the low temperature region.

We now focus on the origin of the 340 K peak. Before the discussion, we first give an overview of the previous models in titanate perovskites. We note that a similar Debye-like anomaly was found in a number of perovskite materials containing titania in a wide temperature range,[13,14] and was ascribed to a space-charge polarization. Within such a space-charge model, the free carriers are stored at the two dielectric-electrode interfaces. However, in our samples the dielectric behavior follows UDR law. And it is well known that the universal dielectric law is typically valid for materials with hopping localized charge carriers,[9,15] implying that the charge carriers in present work are localized ones instead of free charge carriers. It is therefore unlikely that the space-charge polarization is the origin of the 340 K peak.

Other possible models include the Maxwell-Wagner-type relaxation model and Skanavi's model.[16] The former usually occurs in samples with inhomogeneous microstructure consisting of high-conductive grains and low-conductive grain boundaries. This microstructure can be obtained by the loss of oxygen from the bulk of the grains during the high-temperature sintering and reoxidation of the surface layers of the grain boundaries during the cooling-down processes. The Maxwell-Wagner model was used to explain the 250 K peak very well,[7] but cannot account for the great enhancement of the 340 K peak after annealing the as-prepared sample in N_2 atmosphere. The latter is attributed to the thermally activated Ti^{4+} ions hopping locally in six equivalent minima resulting in the orientated polarization. In present case the 340 K peak is closely related to the oxygen vacancies. As a result, the Skanavi's model cannot be directly adopted to explain the 340 K peak. Furthermore, both models are usually used to explain a relaxation-type process which shows a step in the dielectric constant accompanied by a peak in the corresponding loss tangent. However, in our case, only one peak was observed in the dielectric constant without being accompanied by a peak in the loss tangent, implying that this dielectric peak is unlikely to be caused by a relaxation process.

As mentioned above, a possible model has to consider the following factors: the 340 K peak is not likely to be caused by a relaxation process; the 340 K peak is closely related to the oxygen vacancies; and the dielectric behavior follows the UDR law. It is known that annealing the sample in the reducing atmosphere at high temperatures would increase the concentration of the oxygen vacancies. The ionization of the oxygen vacancies will create the conducting electrons

$$O_o \Leftrightarrow V_o + 1/2 O_2, \tag{3}$$

$$V_o \Leftrightarrow V_o^{\cdot} + e, \tag{4}$$

$$V_o^{\cdot} \Leftrightarrow V_o^{\cdot\cdot} + e, \tag{5}$$

where the Kröger-Vink notation of defects is adopted. $V_o^{\cdot}$ and $V_o^{\cdot\cdot}$ represents the oxygen vacancy carrying one and two excess positive charges respectively. In the perovskite oxides, the activation energy for the first ionization of oxygen vacancies as described in Eq. (4) is 0.1 eV,[17] near the activation energy of 97 meV for the conduction in the low temperature region. This indicates that the first ionization of the oxygen vacancies is responsible for the conduction in the low temperature range. Considering the charge balance, either Ti^{3+} or Cu^{1+} is induced to compensate the existence of oxygen vacancies. Depending on the band structure of CCTO, the Ti^{3+} or Cu^{1+} sites might act as acceptor centers, so that *p*-type carriers are introduced. In addition, at higher temperatures, the motion of oxygen vacancies would be activated. The positively charged oxygen vacancies are also *p*-type carriers. In our case, the activation energy (0.33 eV) for the conduction at high temperatures is much higher than the hopping energy of the electrons between the Ti^{4+} and Ti^{3+} ions in CCTO,[18] but much smaller than that of the motion of the doubly ionized oxygen vacancies (1.1 eV) (Ref. 19) and that of the second ionization of oxygen vacancies (1.4 eV) as described in Eq. (5) in $SrTiO_3$.[20] Therefore, it is most likely that the induced Cu^{1+} ions in the nitrogen-annealed CCTO sample introduces the *p*-type carriers, just like in the copper-containing ferrites.[21] The local oscillation of these *p*-type carriers and electrons (*n*-type carriers) gives rise to the dipolar effect and has contributions to the dielectric polarization. From the comparison of the activation energies for the conduction in the high and low temperature regions, we assume that the mobility of *p* carriers is lower than that of *n* carriers. At lower temperatures, the contribution to the polarization from the *n* carriers is dominating, which is also supported by the measurement of the thermoelectric power.[6] However, at higher temperatures the electrons become less localized, which weakens the dipolar effect, and hence have less contribution to the polarization but have great contribution to the conductivity. This effect results in a near-exponential increase in ε'' (or $\tan\delta$) ($\varepsilon'' \sim \sigma/\omega$) as indicated in Fig. 1. On the contrary, the *p*-type carriers, active at higher temperatures, have predominated contribution to the dielectric polarizations. The extra contribution to the conduction from the *p*-type carriers leads to the great increase in σ near 340 K (Fig. 3). Since the polarization of *p*-type carriers has opposite sign to that of *n*-type carriers;[21] therefore, a dielectric peak can be observed near the transition temperature where the polarization mechanism crossovers from the *n* type to *p* type. This is partly supported by deduced *s* parameters shown in the inset of Fig. 2 in which, for the samples annealed in N_2, the slope of the linear temperature dependence of *s* changes from a negative value to a positive value at the transition temperature. Because the contribution to the polarization from either the *n*- or *p*-type carriers depends strongly on the measured frequencies, the 340 K peak exhibits a thermally activated Debye-like feature. And the appearance of 340 K peak is a competition process depending on the competitive contribution to polarization between *n*- and *p*-type carriers rather than a relaxation process.

In summary, the post-sintering annealing studies on dielectrics of CCTO ceramics have shown that apart from the previously reported 250 K peak, an oxygen-vacancy-related dielectric peak was observed near 340 K. This peak exhibits the thermally activated Debye-like feature and can be well understood by considering the collective contributions of the *n*- and *p*-type carriers to the dielectric polarization.

We acknowledge the financial support from National 973 Project of China, National Natural Science Foundation of China (Grant No. 10474050), and Tsinghua University Natural Science Foundation. This work was also supported in part by China Postdoctoral Science Foundation.

---

*Corresponding author. Electronic mail: lwzhang@tsinghua.edu.cn

[1] J. E. Schooley, W. R. Hosler, and M. L. Cohen, Phys. Rev. Lett. **12**, 474 (1964).

[2] M. A. Subramanian, D. Li, N. Duan, B. A. Reisner, and A. W. Sleight, J. Solid State Chem. **151**, 323 (2000).

[3] A. P. Ramirez, M. A. Subramanian, M. Gardel, G. Blumberg, D. Li, T. Vogt, and S. M. Shapiro, Solid State Commun. **115**, 217 (2000).

[4] C. C. Homes, T. Vogt, S. M. Shapiro, S. Wakimoto, and A. P. Ramirez, Science **293**, 673 (2001).

[5] B. A. Bender and M.-J. Pan, Mater. Sci. Eng., B **117**, 339 (2005).

[6] S. Y. Chung, I. D. Kim, and S. J. L. Kang, Nat. Mater. **3**, 774 (2004).

[7] C. C. Wang and L. W. Zhang, Appl. Phys. Lett. **88**, 042906 (2006).

[8] L. Chen, C. L. Chen, Y. Lin, Y. B. Chen, X. H. Chen, R. P. Bontchev, C. Y. Park, and A. J. Jacobson, Appl. Phys. Lett. **82**, 2317 (2003).

[9] A. K. Jonscher, *Dielectric Relaxation in Solids* (Chelsea Dielectrics Press, London, 1983).

[10] A. Tselev, C. M. Brooks, S. M. Anlage, H. Zheng, L. Salamanca-Riba, R. Ramesh, and M. A. Subramanian, Phys. Rev. B **70**, 144101 (2004).

[11] G. A. Samara, W. F. Hammetter, and E. L. Venturini, Phys. Rev. B **41**, 8974 (1990).

[12] C. C. Wang, Y. M. Cui, G. L. Xie, C. P. Chen, and L. W. Zhang, Phys. Rev. B **72**, 064513 (2005).

[13] R. Stumpe, D. Wagner, and D. Bäuerle, Phys. Status Solidi A **75**, 143 (1983).

[14] O. Bidault, P. Goux, M. Kchikech, M. Belkaoumi, and M. Maglione, Phys. Rev. B **49**, 7868 (1994).

[15] N. F. Mott and E. A. Davis, *Electronic Processes in Noncrystalline Materials* (Clarendon Press, Oxford, 1979).

[16] G. I. Skanavi and E. N. Matveeva, Sov. Phys. JETP **3**, 905 (1957).

[17] J. Daniels and K. H. Hardtl, Philips Res. Rep. **31**, 480 (1976).

[18] L. Zhang and Z. J. Tang, Phys. Rev. B **70**, 174306 (2004).

[19] R. Waser, T. Baiatu, and K. H. Hardtl, J. Am. Ceram. Soc. **73**, 1645 (1990).

[20] S. A. Long and R. N. Blumenthal, J. Am. Ceram. Soc. **54**, 577 (1971).

[21] N. Rezlescu and E. Rezlescu, Phys. Status Solidi A **23**, 575 (1974).