01 Mar 2007

Dielectric Response of Sr Doped $CaCu_3Ti_4O_{12}$ Ceramics

Wei Li

Robert W. Schwartz
Missouri University of Science and Technology

Aiping Chen

Jinsong Zhu

Recommended Citation

W. Li et al., "Dielectric Response of Sr Doped $CaCu_3Ti_4O_{12}$ Ceramics," *Applied Physics Letters*, American Institute of Physics (AIP), Mar 2007.
The definitive version is available at https://doi.org/10.1063/1.2713167

APPLIED PHYSICS LETTERS **90**, 112901 (2007)

Dielectric response of Sr doped $CaCu_3Ti_4O_{12}$ ceramics

Wei Li[a] and Robert W. Schwartz[b]
Department of Materials Science and Engineering, University of Missouri-Rolla, Rolla, Missouri 65409

Aiping Chen and Jinsong Zhu
National Laboratory of Solid State Microstructures, Department of Physics, Nanjing University, Nanjing 210093, People's Republic of China

(Received 27 December 2006; accepted 6 February 2007; published online 12 March 2007)

$Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ (x=0, 0.1, and 0.2) ceramics were fabricated and their dielectric properties were investigated. It was found that the dielectric constant significantly decreased with the increase of Sr content at low temperature region (<250 K) and remained almost unchanged at high temperature region (>250 K). Three sets of relaxation peaks were observed in electric modulus plots, which were considered to be associated with grains, domain boundaries, and grain boundaries, respectively. Through the analysis of the heights and calculated activation energies of the relaxation peaks, it is strongly believed that the suppressed dielectric constant is related to the change of domain boundaries with Sr doping. © *2007 American Institute of Physics*.
[DOI: 10.1063/1.2713167]

The perovskite-related structure of $CaCu_3Ti_4O_{12}$ (CCTO) was reported to have a giant dielectric constant ($>10^4$) in ceramics, single crystals, and thin films, despite the fact that the dielectric constant calculated from the polarizabilities of the constituent atoms using the Clausius-Mossotti relation is only ~ 50.[1–6] This high dielectric constant shows weak temperature dependence over the wide temperature range of 100–300 K but drops abruptly to ~ 100 below 100 K with neither a phase transition nor accompanying long-range crystal structure change. The decrease in dielectric constant demonstrates a typical Debye-type relaxation behavior.

The notable physical features in CCTO are scientifically interesting and have attracted extensive investigations regarding the origin of the enormously large dielectric permittivity. Typical explanations for the observed permittivity response include local dipole moments that are associated with off-center displacement of Ti ions,[1] relaxorlike dynamical slowing of dipolar fluctuations in nanosize domains,[2] collective ordering of local dipole moments,[3] spatial inhomogeneity of local dielectric response,[4] electrode depletion effects,[5] and grain boundary (internal) barrier layer capacitance (IBLC) mechanisms.[6] Today, the origin of the giant dielectric response is still ambiguous, and the IBLC explanation associated with an extrinsic mechanism seems mostly likely, since no noticeable evidence has been found for either intrinsic lattice or electronic-based mechanisms from first principles calculations.[7]

In the IBLC mechanism, the insulating grain boundary layers between semiconducting grains act as electrostatic barrier layers blocking the current flow.[8] In this model, the effective permittivity can be estimated by $\varepsilon_{\mathrm{eff}} \sim \varepsilon_{\mathrm{gb}}(t_{\mathrm{g}}/t_{\mathrm{gb}})$, where $\varepsilon_{\mathrm{gb}}$ is the relative permittivity of the grain boundary phase, t_{g} is the average grain size, and t_{gb} is the average thickness of the grain boundaries. However, a contradictive problem related to this mechanism is that CCTO single crystals also possess large permittivity without insulating grain boundaries. This fact strongly indicates that other kinds of barriers to conductivity exist within the crystals in the form of defects. Some researchers consider twin boundaries as a type of insulating barrier layer inside the single crystals (CCTO crystals are twinned on a microscopic level with essentially the same density of twins in different orientations[1,9]). However, Wu *et al.*[10] declared that they did not find the presence of twin domains by transmission electron microscopy (TEM) in single crystals. Instead, a high density of dislocations as well as regions with cation disorder and planar defects was observed, which serve as internal barrier layers.

Most recently, domain boundaries were proposed as another kind of insulating barrier layer in these materials. Domains are easily developed in large grains and the insulating character of the domain boundaries was attributed to the ordered arrangement of dislocations (in contrast, the insulating character of the grain boundaries was attributed to the segregation of Cu ions).[11] Chung's[12] observation by TEM suggests that grains consist of thick domain boundaries and domains, whose zone axes are tilted away from each other at an angle of $<1°$. Such a slight misfit between domains may cause lattice distortion, resulting in the presence of lattice strain and misfit dislocations. Whangbo and Subramanian[13] even proposed a structural model of planar defects, resulting from twinning parallel to the (110), (010), and (001) planes, to explain the probable origin of domain boundaries. By performing impedance analysis, Shao *et al.*[14] detected the electrical response associated with insulating domain boundaries in addition to that associated with grains and grain boundaries. However, as supplementary insulating barrier layers in CCTO, investigations of domain boundaries are only beginning; more experimental observations addressing their presence and their contribution to the high permittivity are urgently needed.

In this letter, three sets of electrical responses were observed in electric modulus plots as a function of temperature. By substituting Sr onto the Ca site of CCTO, the peak

---

[a] Present address: Max-Planck-Institute of Microstructure Physics, Halle, Germany; electronic mail: whilylee@gmail.com

[b] Author to whom correspondence should be addressed; FAX: 573-341-6934; electronic mail: rwschwar@umr.edu

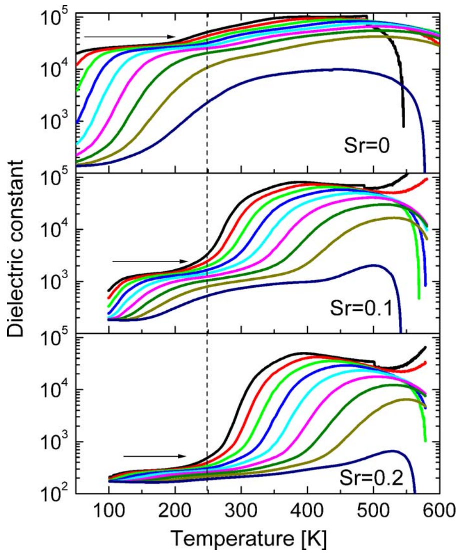

FIG. 1. (Color online) Dielectric constant as a function of temperature for various frequencies of 10^2, $10^{2.5}$, 10^3, $10^{3.5}$, 10^4, $10^{4.5}$, 10^5, $10^{5.5}$, and 10^6 Hz for $Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ ($x=0$, 0.1, and 0.2), respectively.

heights and activation energies of the electrical responses were correspondingly changed, and a significant suppression of the dielectric constant in low temperature region occurred. A possible reason for this behavior is briefly discussed based on the experimental observations.

$Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ ($x=0$, 0.1, and 0.2) ceramics were fabricated by calcination of high purity $CaCO_3$, $SrCO_3$, CuO, and TiO_2 at 800 °C for 12 h followed by sintering in air at 1050 °C for 17 h using a conventional solid state reaction method. The dielectric properties of the ceramics were measured using an HP4194A impedance analyzer in the frequency range from 100 Hz to 1 MHz and over the temperature range from 100 to 600 K.

Figure 1 shows the dielectric constant of CCTO ceramics with different Sr doping contents as a function of temperature at various frequencies. Two easily distinguishable regions may be identified by the dotted line that is indicated at ~250 K. The values of dielectric constant in the low temperature region were significantly depressed by Sr doping while those in the high temperature region remained almost unchanged. The electrical responses in the high temperature region may be attributed to the migration of excited electrical particles at high temperatures. A detailed description of the associated conduction behavior goes beyond the theme of this letter. Rather, attention is focused on the greatly suppressed dielectric constant in the low temperature region from ~10 000 at $x=0$ to ~1000 at $x=0.1$ and ~200 at $x=0.2$. Further increases of doping content up to $x=1.0$ only result in slight additional decreases in dielectric constant to ~180.[15]

Figures 2(a)–2(c) depict the temperature dependence of the dielectric loss of CCTO ceramics with different Sr contents. Clearly, two sets of relaxation peaks may be observed in all of the samples. It may also be noted that the peak temperatures shift to higher values with an increase of the measurement frequency. Additionally, with increasing Sr content, peak heights of the first set gradually decrease while those of the second set increase. By using an Arrhenius expression,

$$f = f_0 \exp(-E_a/k_B T),$$

where E_a is the activation energy and k_B is the Boltzmann parameter, activation energies for the first and second sets of relaxation processes were calculated to be 49.6, 120.9, and 131.3 meV and 0.44, 0.53, and 0.53 eV for $x=0$, 0.1, and 0.2, respectively. The obtained value of 49.6 meV is very close to the previously reported value for CCTO single crystals (54 meV in Ref. 2).

In order to explore the observed electrical responses in Sr doped CCTO, dielectric data were replotted in electric

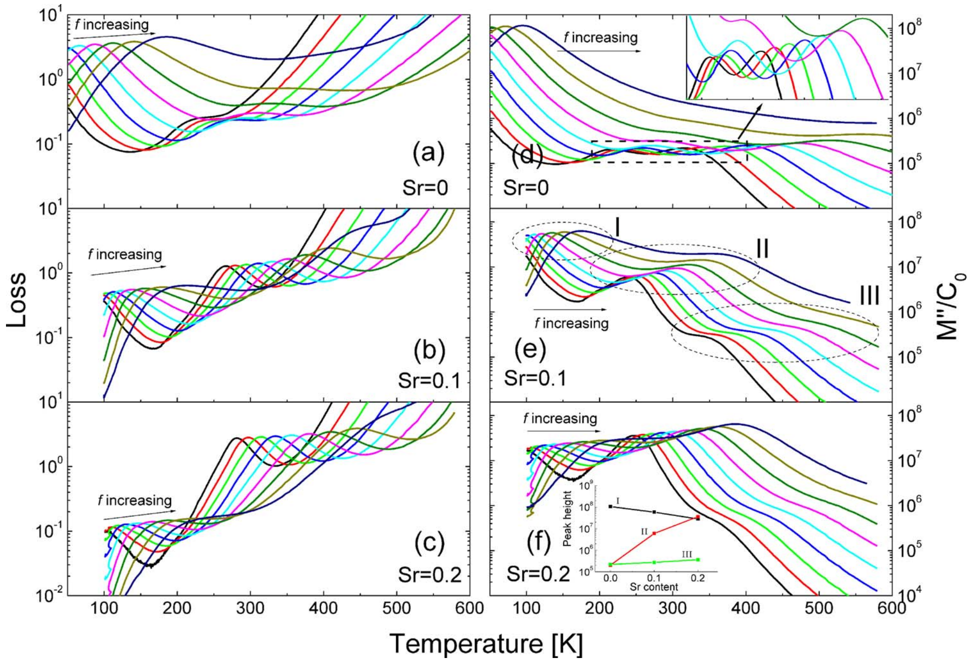

FIG. 2. (Color online) Dielectric loss [(a)–(c)] and electric modulus [(d)–(f)] as a function of temperature for various frequencies of 10^2, $10^{2.5}$, 10^3, $10^{3.5}$, 10^4, $10^{4.5}$, 10^5, $10^{5.5}$, and 10^6 Hz for $Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ ($x=0$, 0.1, and 0.2), respectively. The upper inset is the enlarged part of dashed rectangle area. The bottom inset shows the peak heights vs Sr content.

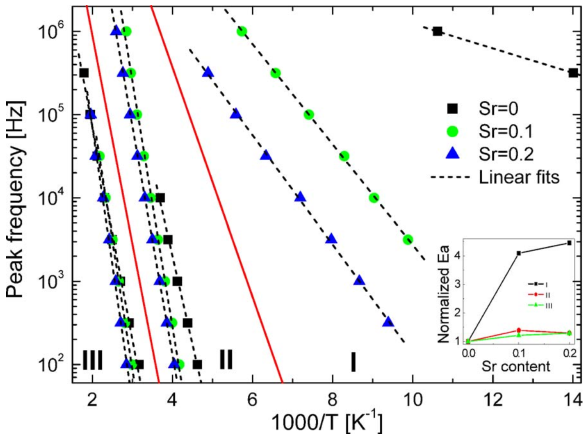

FIG. 3. (Color online) Three sets of peak frequencies as a function of temperature for $Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ with $x=0$, 0.1, and 0.2. Slopes from the linear fits yield the values of activation energies. The inset shows the normalized activation energies vs Sr content for the three sets of relaxation processes.

modulus formalism, as shown in Figs. 2(d)–2(f). The upper inset shows the enlarged part of dashed rectangle area in Fig. 2(d). Apparently, three sets of electrical responses (I, II, and III) may be clarified as indicated by the dashed line ellipses in Fig. 2(e). The bottom inset shows the variation of their peak heights with Sr contents at a measurement frequency of 1 kHz. The peak heights of sets I, II, and III are slightly decreased, significantly increased, and almost unchanged, respectively, with increasing Sr content. Moreover, the entire peak temperatures shift to higher values with increasing frequency and remain almost unchanged with x, except for a slight increase for the set I peaks with initial Sr doping.

Figure 3 illustrates the Arrhenius plots for all thermally excited relaxation processes in CCTO with various Sr contents. Activation energies obtained from the slopes of linear fits were determined to be 29.4, 120.4, and 131.1 meV for set I, 0.42, 0.59, and 0.55 eV for set II, and 0.51, 0.62, and 0.66 eV for set III, with $x=0$, 0.1, and 0.2, respectively. It may be noticed that Sr doping in CCTO results in a significant increase in activation energy values for set I and a relatively slight increase in activation energy values for sets II and III. This tendency of activation energies becomes more evident from the normalized activation energy plot, as shown in the inset of Fig. 3.

Since domain boundaries and grain boundaries were suggested (and observed) to be two kinds of insulating layers inside CCTO, we feel it is reasonable that the three sets of relaxation peaks be attributed to grains, domain boundaries, and grain boundaries, respectively. In fact, our recent investigations[16] indicate that the resistance and capacitance associated with set II remain constant while those associated with set III gradually decrease with applied dc voltage. The different behavior makes it easy to distinguish the electrical response of grain boundaries from that of domain boundaries according to the published results.[17] Reconsidering the experimental results, it may be noticed that with increasing Sr doping content, as the dielectric constant significantly decreased, the peak heights of set II significantly increased, the peak heights of set I slightly decreased, and the peak heights of set III remained essentially unchanged. Peak temperatures remain unchanged with x except for the slight shift with initial Sr doping. Viewed collectively, these results provide clues that the significantly suppressed dielectric constant (in the low temperature region) by Sr doping is associated with changes in domain and domain boundary character. Effects of grain boundaries are minimal. This interpretation is pursued further below.

In CCTO, the TiO_6 octahedra are tilted to form a square planar coordination for Cu.[1,2] The framework is very rigid and the space for the A site cation is highly restricted. Based on ionic radii,[18] the expected Ca–O distance is 2.72 Å, while the observed distance is 2.61 Å.[1] This means that Ca ions on the A site are under compression. The ionic radius of Sr is much larger than that of Ca, and the Sr–O distance is expected to be 2.82 Å. In contrast, the observed Sr–O distance is 2.64 Å. Due to the larger ionic radius of Sr compared to Ca, stoichiometric $SrCu_3Ti_4O_{12}$ cannot be formed.[15] Recent investigations revealed that the formation of domain boundaries in large grain ceramics may be attributed to an orderly arrangement of dislocations,[11] and the slight misfit between domains may in turn cause lattice distortion, lattice strain, and misfit dislocations.[12] By substituting Sr for Ca (in this letter, 10% and 20% contents) on the A site of CCTO, the much larger Sr stretches the Ti–O bonds and affects the tilted TiO_6 octahedra, resulting in a change of domains and domain boundaries. This explanation is in agreement with our observations in the electric modulus plot and the calculated activation energies and indicates that domain boundaries are sometimes more important than grain boundaries as insulating layers in defining the high permittivity response observed for CCTO.

This work was supported by a MURI Program sponsored by the Office of Naval Research under Grant No. N000-14-05-1-0541 and the National Natural Science Foundation of China under Grant No. 90207027.

[1] M. A. Subramanian, D. Li, N. Dunn, B. A. Reisner, and A. W. Sleight, J. Solid State Chem. **151**, 323 (2000); M. A. Subramanian and A. W. Sleight, Solid State Sci. **4**, 347 (2002).

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

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

[4] M. H. Cohen, J. B. Neaton, L. He, and D. Vanderbilt, J. Appl. Phys. **94**, 3299 (2003).

[5] P. Lunkenheimer, R. Fichtl, S. G. Ebbinghaus, and A. Loidl, Phys. Rev. B **70**, 172102 (2004).

[6] D. C. Sinclair, T. B. Adams, F. D. Morrison, and A. R. West, Appl. Phys. Lett. **80**, 2153 (2002).

[7] L. He, J. B. Neaton, M. H. Cohen, D. Vanderbilt, and C. C. Homes, Phys. Rev. B **65**, 214112 (2002); L. He, J. B. Neaton, D. Vanderbilt, and M. H. Cohen, *ibid.* **67**, 012103 (2003).

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

[9] J. Li, A. W. Sleight, and M. A. Subramanian, Solid State Commun. **135**, 260 (2005).

[10] L. Wu, Y. Zhu, S. Park, S. Shapiro, and G. Shirane, Phys. Rev. B **71**, 014118 (2005).

[11] T. T. Fang and H. K. Shiau, J. Am. Ceram. Soc. **87**, 2027 (2004).

[12] S. Y. Chung, Appl. Phys. Lett. **87**, 052901 (2005).

[13] M. H. Whangbo and M. A. Subramanian, Chem. Mater. **18**, 3257 (2006).

[14] S. F. Shao, J. L. Zhang, P. Zheng, W. L. Zhong, and C. L. Wang, J. Appl. Phys. **99**, 084106 (2006).

[15] J. Li, M. A. Subramanian, H. D. Rosenfeld, C. Y. Jones, B. H. Toby, and A. W. Sleight, Chem. Mater. **16**, 5223 (2004).

[16] W. Li and R. W. Schwartz, Appl. Phys. Lett. **89**, 242906 (2006); W. Li and R. W. Schwartz, Phys. Rev. B **75**, 012104 (2007).

[17] T. B. Adams, D. C. Sinclair, and A. R. West, Phys. Rev. B **73**, 094124 (2006).

[18] R. D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **32**, 751 (1976).