Ti-rich and Cu-poor grain-boundary layers of CaCu3Ti4O12 detected by x-ray photoelectron spectroscopy

C Wang
Zhejiang University, caow@uow.edu.au

H J. Zhang
Zhejiang University

P M. He
Zhejiang University

G H. Cao
Zhejiang University

Follow this and additional works at: https://ro.uow.edu.au/engpapers

Part of the Engineering Commons
https://ro.uow.edu.au/engpapers/5146

Recommended Citation
Wang, C; Zhang, H J.; He, P M.; and Cao, G H.: Ti-rich and Cu-poor grain-boundary layers of CaCu3Ti4O12 detected by x-ray photoelectron spectroscopy 2007.
https://ro.uow.edu.au/engpapers/5146

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au
Ti-rich and Cu-poor grain-boundary layers of CaCu3Ti4O12 detected by x-ray photoelectron spectroscopy
C. Wang, H. J. Zhang, P. M. He, and G. H. Cao

Citation: Appl. Phys. Lett. 91, 052910 (2007); doi: 10.1063/1.2768006
View online: http://dx.doi.org/10.1063/1.2768006
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v91/i5
Published by the American Institute of Physics.

Related Articles
Self-assembled NaNbO3-Nb2O5 (ferroelectric-semiconductor) heterostructures grown on LaAlO3 substrates
Appl. Phys. Lett. 101, 132902 (2012)
Pressure and electric field effects on piezoelectric responses of KNbO3
J. Appl. Phys. 112, 064106 (2012)
Enhanced piezoelectric properties of (Na0.5+y+zK0.5−y)(Nb1−xTax)O3 ceramics
Appl. Phys. Lett. 101, 012902 (2012)
Multiferroic response of nanocrystalline lithium niobate
J. Appl. Phys. 111, 07D907 (2012)
Non-radiative complete surface acoustic wave bandgap for finite-depth holey phononic crystal in lithium niobate
Appl. Phys. Lett. 100, 061912 (2012)

Additional information on Appl. Phys. Lett.
Journal Homepage: http://apl.aip.org/
Journal Information: http://apl.aip.org/about/about_the_journal
Top downloads: http://apl.aip.org/features/most_downloaded
Information for Authors: http://apl.aip.org/authors

ADVERTISEMENT
Ti-rich and Cu-poor grain-boundary layers of CaCu$_3$Ti$_4$O$_{12}$ detected by x-ray photoelectron spectroscopy

C. Wang, H. J. Zhang, P. M. He, and G. H. Cao$^{a}$

Department of Physics, Zhejiang University, Hangzhou 310027, People’s Republic of China

(Received 27 June 2007; accepted 11 July 2007; published online 2 August 2007)

Cleaved and polished surfaces of CaCu$_3$Ti$_4$O$_{12}$ ceramics have been investigated by x-ray photoelectron spectroscopy (XPS) and energy dispersive x-ray spectroscopy (EDX), respectively. While EDX technique shows the identical CaCu$_3$Ti$_4$O$_{12}$ stoichiometry for the two surfaces, XPS indicates that the cleaved surface with grain-boundary layers is remarkably Ti-rich and Cu-poor. The core-level spectrum of Cu 2$p$ unambiguously shows the existence of monovalent copper only for the cleaved surface. Possible grain-boundary structure and its formation are discussed. © 2007 American Institute of Physics. [DOI: 10.1063/1.2768006]

CaCu$_3$Ti$_4$O$_{12}$ (CCTO) has recently attracted considerable interest due to its extraordinarily high dielectric permittivity (~10,000) at low frequencies over a wide temperature range (100–400 K). The giant dielectric phenomenon has been primarily elucidated as an intrinsic effect in terms of an internal-barrier-layer-capacitor mechanism. It was suggested and then confirmed that grain boundary (GB) was the internal barrier for CCTO ceramics. As for CCTO crystals which show even larger dielectric permittivity, internal barriers were still inferred from impedance spectroscopy measurement. In fact, CCTO ceramics contain domain boundaries as well as grain boundaries, revealed by scanning electron microscopy and high-resolution transmission electron microscopy. As a result, the detailed dielectric responses of CCTO ceramics can be well interpreted by using a double-barrier-layer-capacitor model.

So far, however, the structure of the internal barriers (grain boundaries and domain boundaries) remains unclear. It was initially suggested that twin boundary was the possible barrier layer. A structural model of planar defects due to a twinning parallel to [100] planes was recently proposed, yet it needs further experimental support. According to a detailed transmission electron microscopy investigation, such twin domains could not be detected in single crystals or polycrystals; instead, high density of dislocations and cation-disorder-induced planar defects were observed. Very recently, x-ray diffraction under extremely high hydrostatic and uniaxial compression suggested that CCTO ceramics were composed of grains with stiffer shells and softer cores. If so, the GB layers should be different from the grain interiors in structure and composition. However, another recent report on Mn-doping effect proposed that the grain and GB regions in CCTO ceramics might consist of the same phase but with slightly different compositions.

In this letter, x-ray photoelectron spectroscopy (XPS) and energy dispersive x-ray spectroscopy (EDX) were employed to detect the possible differences between a polished surface (PS) and a cleaved surface (CS) of CCTO ceramic samples. For a CS, GB layers remain on the surface because of the relatively weak linkage between grains. In the case of a PS, on the other hand, grain interiors are exposed on the surface. Because the detecting depth of XPS is ~1 nm in most cases, XPS actually reveals the information of ultrathin surface layers. In comparison, the information depth of EDX is commonly at the micron scale, thus EDX measures the bulk composition. By examining the CS and PS layers with the two techniques, one may obtain the compositional and structural information, especially for the GB layers.

The CCTO ceramic samples were prepared by conventional solid-state reaction using the powdered chemicals of TiO$_2$ (99.99%), CaCO$_3$ (99.99%), and CuO (99.99%). The starting materials were weighed according to the stoichiometric ratio and mixed thoroughly in an agate mortar. The mixed powder was calcined at 1273 K for 12 h in air. This procedure was repeated for three times to ensure that the samples were in single CCTO phase. Then the calcined powder was pressed into a disk ($d$ 12 × 2 mm$^2$) and a rod ($d$ 12 × 15 mm$^2$). The pressed specimens were finally sintered in air at 1353 K for 24 h followed by furnace cooling to room temperature. X-ray diffraction identified single phase for the two specimens. Dielectric measurement with an Agilent 4284A precision LCR meter confirmed that the samples showed the property of giant dielectric permittivity as reported elsewhere.

Prior to the XPS and EDX measurements, the as-prepared CCTO samples were treated to make a PS and a CS, respectively. For the PS sample, the sintered disk was polished by using CeO$_2$ fine powder, followed by removing the remaining CeO$_2$ with a mixture of nitric acid and hydrogen peroxide. Then it was in turn cleaned in distilled water, ethanol, and acetone with a ultrasonic cleaner. The CS sample was obtained simply by cleaving the rod. As soon as the surface was made, the specimen (mounted on a sample holder) was transferred into the ultrahigh vacuum system equipped with an x-ray generator (Mg K$_\alpha$, 1253.6 eV) and an Omicron EAC2000-125 analyzer. The shift of core-level spectra due to the charging effect was calibrated using the contaminated C 1$s$ peak located at 284.6 eV. The XPS intensity was calculated based on the areas of the related peaks. After the XPS experiment, the identical samples were also examined by employing a field-emission scanning electron microscope (SEM) (sirion FEI, Netherlands) equipped with a Phoenix (EDAX) x-ray spectrometer. The samples were coated with very thin layer of gold before they were placed into the SEM chamber.

$^{a}$Author to whom correspondence should be addressed; electronic mail: ghcao@zju.edu.cn
Figure 1 shows the SEM images of the cleaved and polished surfaces of CCTO ceramics. The CS image shows grain-packed morphology with the grain size of ~6 μm. One can see that the cleaving takes place mostly at the grain boundaries. For the PS image, a flat surface is shown except for some cavities. This indicates that the grain interiors show up due to the polishing. It is also noted that both surfaces have very similar EDX spectra, as shown in the insets of Fig. 1. Quantitative analysis indicates that the atomic ratios for CS and PS are 1.0:3.1:4.0 and 1.0:3.0:3.8, respectively, consistent with the stoichiometric ratio of CCTO within the experimental errors (≤5%). Since the information depth is only about 1 nm, the XPS result of the CS reveals the information of the GB layers. Therefore, we conclude that the GB layers are Ti rich and Cu poor, compared with the CCTO stoichiometry.

Figure 3 separately shows the Cu 2p core-level spectra of CCTO ceramics. As can be seen, there is a shoulder at lower energy side of the main peak of 2p only for the CS specimen. By separating the peaks one obtained a small peak at 932.2 eV, suggesting the existence of Cu(I) at GB similar peak separating for the PS specimen was unsuccessful. Another evidence for the existence of Cu(I) comes from the intensities of the Cu 2p shake-up peaks. The CS sample shows relatively weak shake-up peaks, because Cu(I) has no such component. One notes that the amount of excessive Ti is almost equal to the amount of the missing Cu for the CS. This result suggests that some Ti may replace Cu in the GB layers. In
fact, evidence of Ti on the Cu site was given in nonstoichiometric $\text{Sr}_{0.946}(\text{Cu}_{2.946}\text{Ti}_{0.054})_4\text{O}_{12}$ (Ref. 14) and $\text{Na}(\text{Cu}_{2.5}\text{Ti}_{0.5})_4\text{O}_{12}$ (Ref. 15). In CCTO, however, the Ti on the Cu site is far too small to be detected by refining site occupancies from neutron diffraction data. 14 Nevertheless, there is a possibility for the GB in which significant amount of Ti occupies the Cu site. The Ti-for-Cu substitution results in monovalent copper due to the charge neutrality, in agreement with the existence of Cu(I) only for the GB layers.

With the clue of Ti on Cu site, Li et al. 14 proposed a convincing explanation of how CCTO develops conducting regions. At high temperature, Cu(II) reduces to Cu(I) accompanying with a charge compensation via a slight substitution of Ti(IV) on Cu site, forming $\text{Ca}(\text{Cu}_{2+3}\text{Cu}_{2+\text{Ti}^{2+}}\text{Ti}^{4+})_3\text{Ti}_4\text{O}_{12}$. Upon cooling, the Cu(I) converts to Cu(II), liberating electrons into the Ti 3d conduction band. Although this mechanism explains the conductivity of CCTO grains, one could not understand the formation of internal barriers. We notice that the above mechanism ignores the cation migrations during the cooling process. It is possible that the Ti at Cu site migrates to GB layers and domain-boundary layers when cooling down, which forms Ti-rich and Cu-poor barrier layers.

It is also noted that the structure model proposed by Wu et al. 9 is consistent with the result of Ti-for-Cu substitution in GB layers. The planar defect model involves a lattice shift $R_0 = \frac{1}{2}[110]$. 16 Such a lattice shift naturally results in cation disorder in Ca/Cu site, accommodating the Ti-for-Cu substitution. The planar defect may give rise to remarkable strain at the boundary, which explains the thermal etching effect within the grains.6 Furthermore, such a domain-boundary may serves as a stiffer layer as suggested by the high-pressure x-ray diffraction result. 10 Finally, due to the lattice discontinuity, ion-disorder and/or ion displacement, the interface may become a barrier layer against the electron conduction.

In summary, we have revealed the subtle differences in composition of the bulk and grain boundary regions in CCTO ceramics by comparing the core-level spectra of cleaved and polished surfaces. The grain boundary contains remarkably more Ti and less Cu than the grain interior does. Moreover, only the grain boundary layer contains monovalent copper. These results provide crucial insight for the origin of the special giant dielectric phenomenon as well as the grain-boundary structure in CCTO system.

This work was supported by National Science Foundation of China (Grant No. 10274070).

References

1M. A. Subramanian, D. Li, N. Duan, B. A. Reisner, and A. W. Sleight, J. Solid State Chem. 151, 323 (2000).
2C. C. Homes, T. Vogt, S. M. Shapiro, S. Wakimoto, and A. P. Ramirez, Science 293, 673 (2001).
3Derek C. Sinclair, Timothy B. Adams, Finlay D. Morrison, and Anthony R. West, Appl. Phys. Lett. 80, 2153 (2002).
4S. Y. Chung, I. D. Kim, and S. J. L. Kang, Nat. Mater. 3, 774 (2004).
5J. Li, A. W. Sleight, and M. A. Subramanian, Solid State Commun. 135, 260 (2005).
6T. T. Fang and C. P. Liu, Chem. Mater. 17, 5167 (2005).
7Guanghan Cao, Lixin Feng, and Cao Wang, J. Phys. D 40, 2899 (2007).
8M.-H. Whangbo and M. A. Subramanian, Chem. Mater. 18, 3257 (2006).
9L. Wu, Y. Zhu, S. Park, S. Shapiro, G. Shirane, and J. Tafro, Phys. Rev B 71, 014118 (2005).
10Yanzhang Ma, Jianjun Liu, Chunxiao Gao, W. N. Mei, Allen D. White, and Jahan Rasty, Appl. Phys. Lett. 88, 191903 (2006).
11Ming Li, Antonio Feteira, Derek C. Sinclair, and Anthony R. West, Appl. Phys. Lett. 88, 232903 (2006).
12S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Interface Anal. 17, 911 (1991).
13D. Dobler, S. Oswald, and K. Wetzig, Anal. Bioanal. Chem. 374, 646 (2002).
14J. Li, M. A. Subramanian, H. D. Rosenfeld, C. Y. Jones, B. H. Toby, and A. W. Sleight, Chem. Mater. 16, 5223 (2004).
15M. Avdeev and V. B. Nalbandyan, Inorg. Chem. 45, 2217 (2006).
16The original model contains an extra oxygen atom at the interface, what is more, two oxygen atoms are much too close. A more reasonable structure for the planar defect can be simply viewed as $\frac{1}{2}[110]$ shear planes, involving edge-sharing TiO$_6$ octahedra.