Available online at www.sciencedirect.com

SciVerse ScienceDirect

Journal of the European Ceramic Society 32 (2012) 1245–1249

www.elsevier.com/locate/jeurceramsoc

Effect of oxygen sintering atmosphere on the electrical behavior of CCTO ceramics

Rong Yu, Hao Xue*, Zeliang Cao, La Chen, Zhaoxian Xiong*

College of Materials, Xiamen University, Xiamen 361005, PR China

Received 11 October 2011; received in revised form 24 November 2011; accepted 26 November 2011
Available online 29 December 2011

Abstract

The $CaCu_3Ti_4O_{12}$ ceramics were sintered in air and pure O_2 atmosphere, respectively, and the effect of pure O_2 atmosphere on the electrical behavior of the $CaCu_3Ti_4O_{12}$ ceramics was investigated. It was found that the dielectric properties of the $CaCu_3Ti_4O_{12}$ ceramics displayed a Debye-like relaxation between 20 Hz and 1 MHz, but the permittivity of the sample sintered in pure O_2 atmosphere was decreased drastically. Moreover, the *I–V* behavior of the ceramic sintered in pure O_2 atmosphere presented a linear feature. With XPS analysis, it was illustrated that the valence of Cu and Ti elements in the $CaCu_3Ti_4O_{12}$ ceramics had obviously been influenced by the O_2 concentration. Based on the experimental comparison of $CaCu_3Ti_4O_{12}$ ceramics sintered in air and pure O_2 atmosphere, it was suggested that the valence of metallic elements and defects played key role for the origin of the giant permittivity and *I–V* nonlinear feature in the $CaCu_3Ti_4O_{12}$ ceramics.

Keywords: $CaCu_3Ti_4O_{12}$ ceramics; Pure O_2 atmosphere; Electrical behavior'

1. Introduction

Much attention had been paid to the CCTO ceramics by many researchers,[1–3] since its phenomenon of giant permittivity was found, as high as about 100,000. Such kinds of materials with high dielectric constant were usually ferroelectric ceramics such as $Pb(Zr_xTi_{1-x})O_3$ (PZT) and $BaTiO_3$, which depended strongly on temperature. However, the dielectric constant of CCTO is almost the same in the range of 100–400 K.[4–6]

Nowadays, it is gradually accepted that this ultra-high dielectric response is not an intrinsic behavior, but attributed to an external mechanism.[7,8] The dielectric response is thought to be associated with one or more potential barrier layers, such as grain boundaries, domain boundaries, or interface polarization effect.[6,9] A model of internal barrier layer capacitance, IBLC, was proposed based on the analysis of the impedance spectroscopy.[3] The existence of insulating grain boundaries has been confirmed,[5] acting as Schottky-type potential barriers in CCTO ceramics.

It was important to note that the dielectric properties of the CCTO samples were extremely scattered, depending on specific preparation process. For example, the dielectric constant of CCTO was increased from 1000 to 10,000 by changing the sintering temperature only from 1000 °C to 1100 °C as indicated by Bender and Pan.[10] Similarly, Adams et al.[3] enhanced the dielectric constant about an order of magnitude by prolonging the sintering time. Most interestingly, the dielectric constant of the CCTO ceramics increased with abnormal grain growth, meanwhile the resistance of grain boundaries decreased.[11,12] Based on a comparison between the ceramic polycrystalline and single crystal structures, it was proposed that the giant permittivity of the CCTO is mainly controlled by the domain boundaries in the grains.[12,13] A proposed twinning defect or dislocation was supported by CCTO single crystal with giant dielectric constant.[9,14] There was, however, no integrate statement about which barrier layer played key role for the giant permittivity, especially for that of ceramic samples.

In order to verify whether and how the defect and valence of CCTO influence its electrical properties, two kinds of CCTO ceramics were sintered in air and pure O_2 atmospheres in this paper. The effect of sintering atmosphere for CCTO ceramics on the permittivity, impedance, and *I–V* behavior of the polycrystalline materials were investigated in details.

---

* Corresponding authors.
E-mail addresses: xuehao@xmu.edu.cn (H. Xue), zxxiong@xmu.edu.cn (Z. Xiong).

0955-2219/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2011.11.039

2. Experimental

Appropriate amounts of high-purity calcium nitrate (99.9% purity), copper(II) nitrate (99.5%), tetrabutyl titanate(IV) ($C_{16}H_{36}O_4Ti$) and citric acid as chemical reagents were used to synthesize CCTO powder. According to a stoichiometric composition, calcium nitrate, copper(II) nitrate were dissolved into distilled water and then dropped into the solution of tetrabutyl titanate, which was stabilized by acrylamide and citric acid in the solution with 1:1 ratio. The mixed precursor solution was then stirred by magnetic stirring for 0.5 h at ambient temperature. After drying at 80 °C in a water bath, a gel was formed, which was then decomposed at a temperature 450 °C in air for 15 min and crushed to a powdered form. The powder was calcined at 800 °C for 4 h in air to form CCTO phase. The CCTO powder was mixed with polyvinyl alcohol binder, and then pressed into pellets of 10 mm in diameter and 2 mm in thickness. These pellets were sintered at 1050 °C in air and in O_2 (99.99% purity) for 10 h, respectively, and then cooled to room temperature in furnace.

Crystal structures of the CCTO ceramics were identified using an automatical X-ray diffractionator (Rigaku 2500, Japan) with Cu Kα1 radiation. Impedance measurements of the samples were performed at 1 V from 20 Hz to 1 MHz by a LCR precision meter (HP 4284A, USA). The microstructures of the ceramics were observed using a scanning electron microscope (Philips XL30, Holland). Current–voltage measurements were taken using a Source-Measure Unit (Keithley 2400, USA). The element valence of the CCTO samples was analyzed by XPS (PHI-Quantum 2000, USA) with Mg Kα radiation (Kα, 1253.6 eV).

3. Results and discussion

XRD patterns of two kinds of CCTO ceramics sintered at different atmosphere are shown in Fig. 1, which illustrated that single perovskite phase was obtained for both samples without noticeable other phases. The peaks of the ceramics matched well with those of standard spectrum of cubic structured CCTO (PDF01-075-1149).[15]

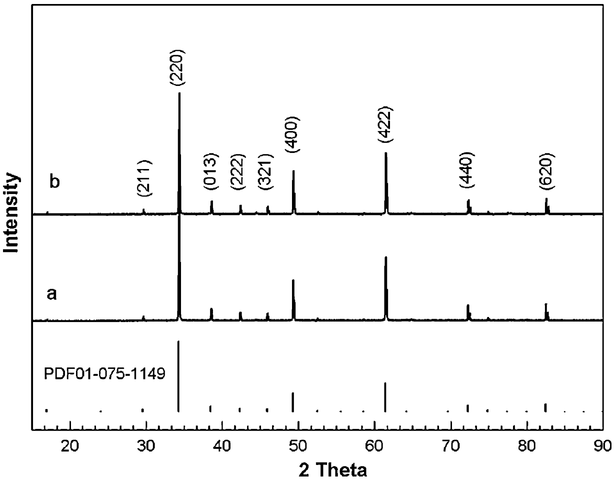

Fig. 1. XRD patterns of CCTO samples sintered at 1050 °C for 10 h in air (a) and in high O_2 partial pressure atmosphere (b), comparing with the reference that corresponds to $CaCu_3Ti_4O_{12}$ obtained from the literature (PDF01-075-1149).

Fig. 2 shows the scanning electron micrograph of the samples. In general, the grains in sample sintered in air are larger than that of the sample sintered in pure O_2. However, the sample sintered in air has fewer pores, which implies it is more compact. The relative density of the sample sintered in air is 96%, and the other sample sintered in pure O_2 is 90%.

Both CCTO samples behaved quite high dielectric permittivity, as shown in Fig. 3, for the frequency dependence of dielectric constant and loss of two kinds of ceramics sintered in different atmospheres. However, the most important difference was that the dielectric constant of the sample sintered in air was 60,000, while those of other samples sintered in oxygen atmosphere was much lower, only about 2000, at the frequency of 1 kHz. With increasing frequency, the dielectric constant of the samples decreased slowly between 100 Hz and 10 kHz, while the dielectric constant decreased drastically when frequency was higher than 10 kHz, corresponding to a peak value of dielectric loss. Therefore, both kinds of ceramics showed typical characteristics of dielectric relaxation, which was in good agreement with that of barrier mechanism reported in literature.[3,5,9,14]

Although the IBLC model had received quite support,[2,3,11] the origin of the inner barrier layer still remained unclear. There

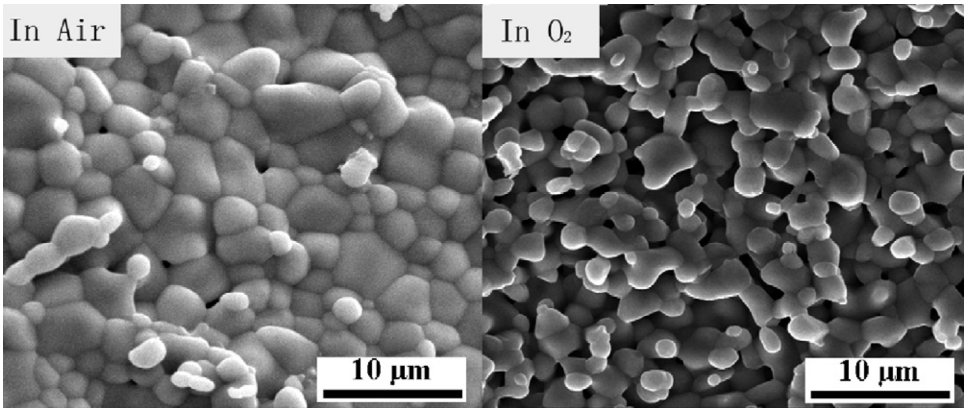

Fig. 2. The scanning electron micrograph of the samples sintered in air and in pure O_2 atmosphere, respectively.

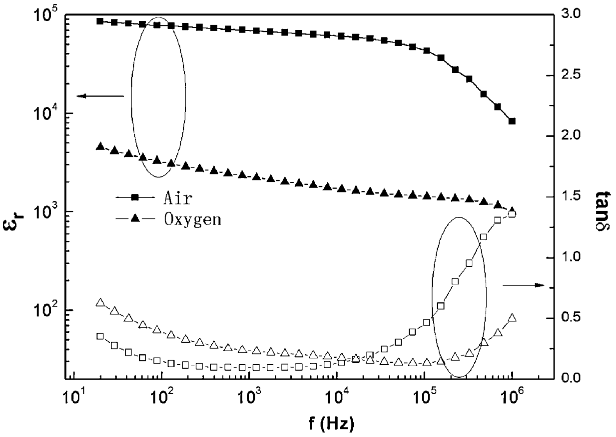

Fig. 3. Frequency dependence of dielectric constant and loss of two kinds of CCTO samples sintered in different atmospheres, at room temperature (25 °C).

were different kinds of suggestions about the location and the form of the barrier layer.[13,16] Fang and Liu[12] have observed internal domains existed in the large grains of CCTO ceramics. But the internal domains were almost invisible in the fine grains. However, the effective dielectric constants for both kinds of the samples only with fine grains were estimated to be in the orders of 10^3 magnitude based on the IBLC model, which was only consistent with the experimental value of the samples sintered in oxygen atmosphere, but was not with that of the sample sintered in air.

In addition, both samples presented a clear Debye type relaxation characteristic in higher frequency, which had almost no relation with the condition of heat treatment for the ceramics, either in air or in oxygen atmosphere. To explain this phenomenon, a hypothesis of nanoscale barrier layer capacitance (NBLC) was suggested by Bueno,[13] and was further confirmed with the experiment results by Ribeiro et al.[17] in which the dielectric constant for the ceramics simultaneously increased with that of grain conductivity.

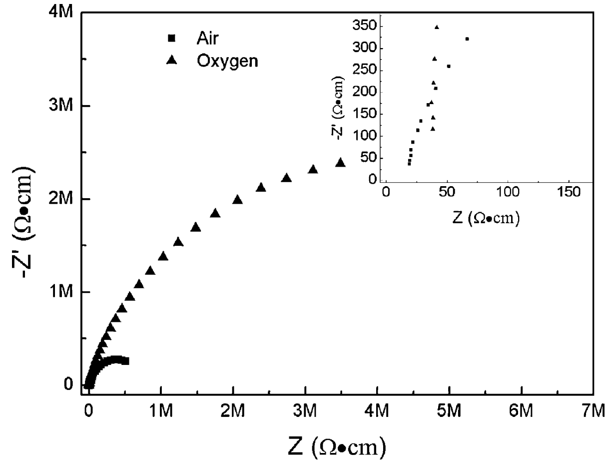

Fig. 4. Impedance complex plane measured at room temperature (25 °C), namely, Z' of both samples sintered at different atmosphere. The inset shows an expanded view of the high frequency data close to the origin.

The complex impedance spectra are shown in Fig. 4, in which there were semi-circular arcs with non-zero intercept on the Z' axis at high frequencies. With the complex impedance analysis

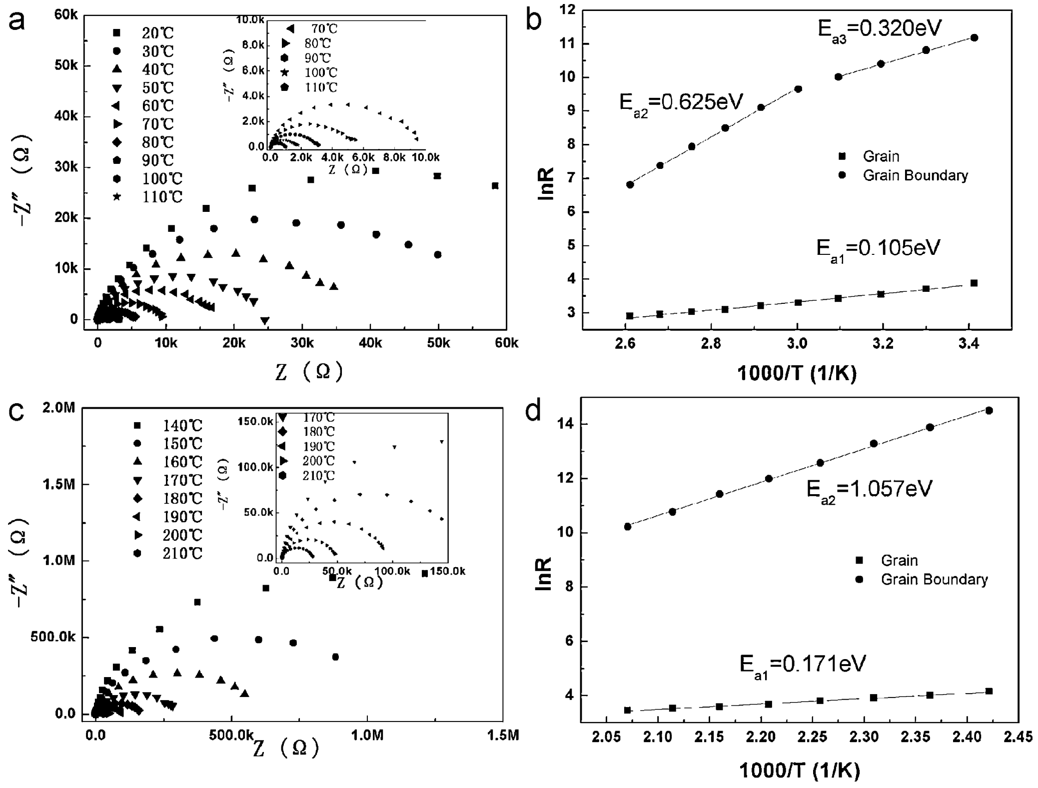

Fig. 5. Temperature dependence of grain and grain boundary conductivity, (a), (b) for the sample sintered in the air, and (c), (d) for the sample sintered in the oxygen atmosphere. The inset in (a) and (c) shows an expanded view of the high frequency data close to the origin.

based on the model of IBLC, internal barrier layer capacitors, the resistance values of grain and grain boundary were 20 Ω cm and 6 kΩ cm for the sample sintered in air, and, 38 Ω cm and 8 MΩ cm for the one sintered in oxygen atmosphere, respectively.

The grain conductivity was weakened for the ceramics sintered in the oxygen atmosphere. And comparing with that of the sample sintered in air, the grain resistances of the sample sintered in the oxygen atmosphere were almost doubled from 20 Ω cm to 38 Ω cm. However, the grain boundary resistance of the sample sintered in the oxygen possesses a remarkably high resistance. The resistance of the grain boundary increased more than 10 times, comparing with that of ceramic sintered in air. Therefore, the grains are less susceptible to the atmosphere than the grain boundaries. This phenomenon could be partially explained by that the semi conductance of grains in CCTO originated from the anti-site defect of Cu/Ca without loss oxygen, which was confirmed not only by the theoretical analysis but also the TEM observation.[18] The concentration of anti-site defects are the main intrinsic defects and far outweigh the concentration of vacancies were also confirmed by the first-principles study.[19]

Moreover, the resistance of the ceramic samples changing with temperature can be expressed as:

$$\rho = \rho_0 e^{(E_a/kT)} \tag{1}$$

where ρ is the resistance of the ceramic sample, ρ_0 is the pre-exponential factor, and E_a is the activation energy. By fitting the Arrhenius plot of ceramic resistance against temperatures, the activation energy of the samples can be figured out (Fig. 5), in which the activation energy of grain is 0.105 eV and 0.171 eV, respectively. There is little difference for the activation energy of grain between the samples. However, the activation energy of grain boundary for the sample sintered in the oxygen is 1.057 eV, which is much higher than that of the sample sintered in air. Furthermore, the Arrhenius plot of the sample sintered in air was not able to be fitted with a straight line, meaning that there was more than one kind of the activation energies in the samples. Actually, the activation energies were 0.320 eV below 70 °C and 0.625 eV above 70 °C, respectively. It was known that large quantities of oxygen vacancies may be resulted for the perovskite structure ceramic materials like $BaTiO_3$ during the sintering process at high temperature.[20] Deep donor levels may be introduced by Ti^{3+} and $Vo^{\bullet\bullet}$ in perovskite structures that were far from the lower level of the conduction band.[21] The captured electrons in the ceramic sample were excited and injected into the conduction band by raising temperature, so as to enhance the electrical conductivity of the CCTO sample. According to the defect model proposed by Whangbo[21] there were the planar defects of Cu^{+}, Ti^{3+} and oxygen vacancy in the form of disorder. The region of grain boundaries was more disordered than that of grains in ceramics. These defects, including oxygen vacancy and low valence cations, were easy to be enriched in the region of grain boundary, which were susceptible to the sintering atmosphere and were closely related with the interface property, such as the conductance and nonlinear *I–V* characteristics of the CCTO ceramics.

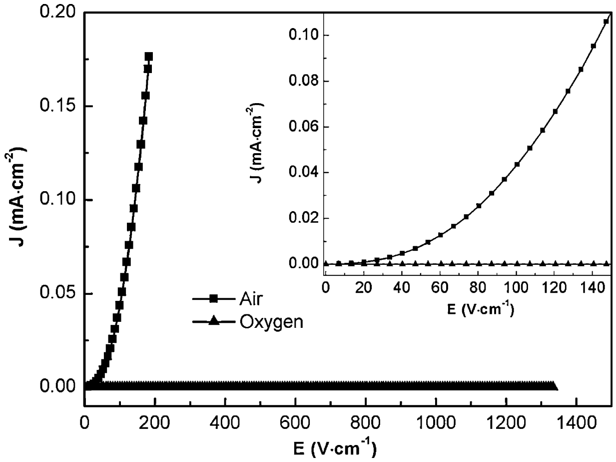

Fig. 6. Plot of current density against electric field for both of the CCTO samples.

The current density–electric field (*J–E*) curves for the two kinds of samples are displayed in Fig. 6. The results indicated that high O_2 partial pressure can induce a significant effect on the *I–V* characteristic of CCTO ceramics. Comparing with the sample sintered in air, a remarkably high resistance and ohmic characteristics were shown in the sample sintered in the oxygen.

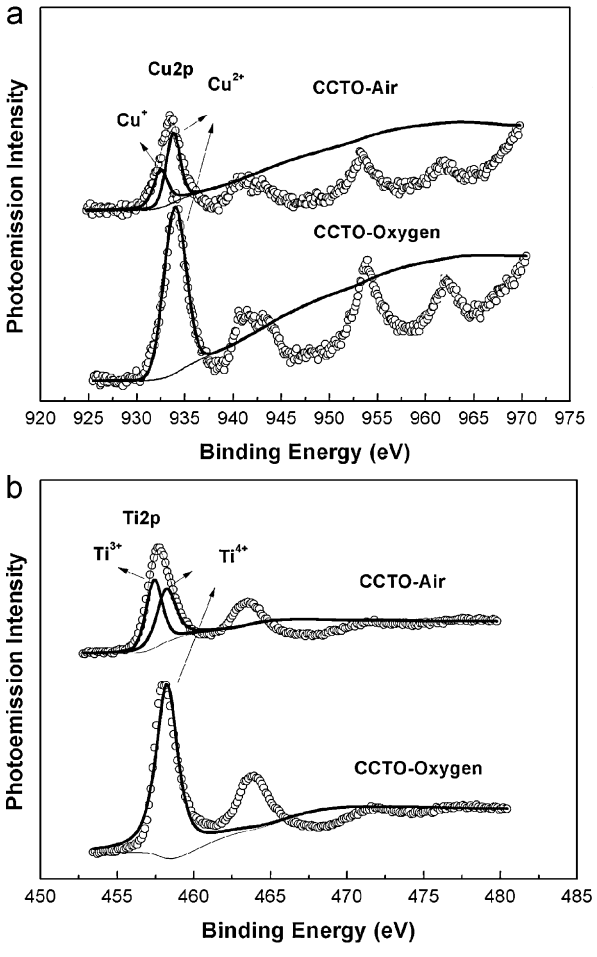

Fig. 7. X-ray photoelectron spectroscopy analysis of the samples sintered in the air atmosphere and in the oxygen atmosphere.

It is reported that the Schottky-type barrier of CCTO formed at grain boundary is dependent of the metal atoms segregated at grain boundary, especially for Cu^+,[22] unlike the more studied varistors such as ZnO and SnO_2, which mainly in regard to the presence of oxygen.[23–25] The low valence cations would be fully oxidized when sintered in an oxygen atmosphere. Thus, the negative charges of acceptors at the boundaries were effectively compensated by the oxygen, resulting in a decrease of conductivity, thereby, decreasing the non-linear electrical properties of the material.

To verify this point, X-ray photoelectron spectroscopy were used to detect the cations valence. The Cu_{2p} and Ti_{2p} XPS curves for both of the samples are shown in Fig. 7 respectively. As to the sample sintered in air, it was shown that the $Cu_{2p3/2}$ and $Ti_{2p3/2}$ peaks can be divided into two peaks by Gaussian–Lorentzian profile fitting. The $Cu_{2p3/2}$ core-level peaks are located at about 932.39 eV and 933.67 eV and the $Ti_{2p3/2}$ core-level peaks are located at about 457.48 eV and 458.11 eV, which is in accordance with Deng.[26] Oppositely, the sample sintered in oxygen shows nearly fully oxidized Cu and Ti ions. The dielectric relaxation and electrical property must have been both affected by the drastically decreased content of Cu^+ and Ti^{3+} ions as discussed above.

4. Conclusions

CCTO ceramics have been sintered at 1050 °C for 10 h in air and in oxygen atmosphere, respectively. We found that the sintering atmosphere of high O_2 partial pressure brought significant influence on the dielectric, impedance and *I–V* characteristics of the CCTO ceramics. Comparing to the CCTO ceramics sintered in air, the CCTO ceramics sintered in pure O_2 possess lower permittivity, higher resistance and linear *I–V* characteristic. It could be confirmed that the high O_2 partial pressure has effectively influenced the valence of the Cu and Ti elements during sintering of CCTO ceramics, combining with the results of XPS analysis. Therefore, the results provided the evidence to prove that the valences of Cu and Ti and the related defects at the grain boundary in CCTO ceramics play key roles for their electrical properties.

Acknowledgements

This work was supported by the Fundamental Research Funds for the Central Universities (Grant No. 2010121052) and Cooperation Foundation offered by The State Key Laboratory of New Ceramics and Fine Processing in Tsinghua University.

References

1. Homes CC, Vogt T, Shapiro SM, Wakimoto S, Ramirez AP. Optical response of high-dielectric-constant perovskite-related oxide. *Science* 2001;**293**:673–6.
2. Subramanian MA, Li D, Duan N, Reisner BA, Sleight AW. High dielectric constant in ACu(3)Ti(4)O(12) and ACu(3)Ti(3)FeO(12) phases. *J Solid State Chem* 2000;**151**:323–5.
3. Adams TB, Sinclair DC, West AR. Giant barrier layer capacitance effects in $CaCu_3Ti_4O_{12}$ ceramics. *Adv Mater* 2002;**14**:1321.
4. Cohen MH, Neaton JB, He LX, Vanderbilt D. Extrinsic models for the dielectric response of $CaCu_3Ti_4O_{12}$. *J Appl Phys* 2003;**94**:3299–306.
5. Chung SY, Kim ID, Kang SJL. Strong nonlinear current–voltage behaviour in perovskite-derivative calcium copper titanate. *Nat Mater* 2004;**3**:774–8.
6. Lunkenheimer Fichtl PR, Ebbinghaus SG, Loidl A. Nonintrinsic origin of the colossal dielectric constants in $CaCu_3Ti_4O_{12}$. *Phys Rev B* 2004;**70**:172102.
7. Lunkenheimer P, Krohns S, Riegg S. Colossal dielectric constants in transition-metal oxides. *Eur Phys J Special Topics* 2010;**180**:61–89.
8. Ferrarelli MC, Sinclair DC, West AR, Dabkowska HA, Dabkowski A, Luke GM. Comment on the origin(s) of the giant permittivity effect in $CaCu_3Ti_4O_{12}$ single crystals and ceramics. *J Mater Chem* 2009;**19**:5916–9.
9. Krohns S, Lunkenheimer P, Ebbinghaus SG, Loidl A. Colossal dielectric constants in single-crystalline and ceramic $CaCu_3Ti_4O_{12}$ investigated by broadband dielectric spectroscopy. *J Appl Phys* 2008;**103**:084107.
10. Bender BA, Pan MJ. The effect of processing on the giant dielectric properties of $CaCu_3Ti_4O_{12}$. *Mater Sci Eng B Solid State Mater Adv Technol* 2005;**117**:339–47.
11. Pan MJ, Bender BA. A bimodal grain size model for predicting the dielectric constant of calcium copper titanate ceramics. *J Am Ceram Soc* 2005;**88**:2611–4.
12. Fang TT, Liu CP. Evidence of the internal domains for inducing the anomalously high dielectric constant of $CaCu_3Ti_4O_{12}$. *Chem Mater* 2005;**17**:5167–71.
13. Bueno PR, Tararan R, Parra R, Joanni E, Ramirez MA, Ribeiro WC, et al. Polaronic stacking fault defect model for $CaCu_3Ti_4O_{12}$ material: an approach for the origin of the huge dielectric constant and semiconducting coexistent features. *J Phys D Appl Phys* 2009;**42**:055404.
14. Li J, Sleight AW, Subramanian MA. Evidence for internal resistive barriers in a crystal of the giant dielectric constant material: $CaCu_3Ti_4O_{12}$. *Solid State Commun* 2005;**135**:260–2.
15. McGuinness C, Downes JE, Sheridan P, Glans PA, Smith KE, Si W, et al. X-ray spectroscopic study of the electronic structure of the high-dielectric-constant material $CaCu_3Ti_4O_{12}$. *Phys Rev B* 2005;**71**:195111.
16. Sarkar S, Chaudhuri BK, Yang HD. Nanostripe domains in $CaCu_3Ti_4O_{12}$: its origin and influences on high permittivity response. *J Appl Phys* 2010;**108**:014114.
17. Ribeiro WC, Joanni E, Savu R, Bueno PR. Nanoscale effects and polaronic relaxation in $CaCu_3Ti_4O_{12}$ compounds. *Solid State Commun* 2011;**151**:173–6.
18. Zhu Y, Zheng JC, Wu L, Frenkel AI, Hanson J, Northrup P, et al. Nanoscale disorder in $CaCu_3Ti_4O_{12}$: a new route to the enhanced dielectric response. *Phys Rev Lett* 2007;**99**:037602.
19. Delugas P, Alippi P, Raineri V. Native point defects in $CaCu_3Ti_4O_{12}$. In: Muralt P, Kosec M, Raineri V, Ravesi S, editors. *Fundamentals and Technology of Multifunctional Oxide Thin Films*. 2010. p. 8.
20. Deng G, Li G, Ding A, Yin Q. Evidence for oxygen vacancy inducing spontaneous normal-relaxor transition in complex perovskite ferroelectrics. *Appl Phys Lett* 2005;**87**:192905.
21. Whangbo MH, Subramanian MA. Structural model of planar defects in $CaCu_3Ti_4O_{12}$ exhibiting a giant dielectric constant. *Chem Mater* 2006;**18**:3257–60.
22. Mei LT, Hsiang HI, Fang TT. Effect of copper-rich secondary phase at the grain boundaries on the varistor properties of $CaCu_3Ti_4O_{12}$ ceramics. *J Am Ceram Soc* 2008;**91**:3735–7.
23. Stucki F, Greuter F. Key role of oxygen at zinc oxide varistor grain boundaries. *Appl Phys Lett* 1990;**57**:446–8.
24. Cox DF, Fryberger TB, Semancik S. Oxygen vacancies and defect electronic states on the SnO_2 (1 1 0)-1 × 1 surface. *Phys Rev B* 1988;**38**:2072–83.
25. Bueno PR, Varela JA, Longo E. SnO_2, ZnO and related polycrystalline compound semiconductors: an overview and review on the voltage-dependent resistance (non-ohmic) feature. *J Eur Ceram Soc* 2008;**28**:505–29.
26. Deng G, Xanthopoulos N, Muralt P. Chemical nature of colossal dielectric constant of $CaCu_3Ti_4O_{12}$ thin film by pulsed laser deposition. *Appl Phys Lett* 2008;**92**:172909.