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Ceramics International 38 (2012) 4217–4220

CERAMICS INTERNATIONAL

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# Dielectric properties of $CaCu_3Ti_4O_{12}$ improved by chromium/lanthanum co-doping

Hamed Ahmadi Ardakani, Morteza Alizadeh *, Rasool Amini, Mohammad Reza Ghazanfari

*Department of Materials Science and Engineering, Shiraz University of Technology, 3619995161 Shiraz, Iran*

Received 3 October 2011; accepted 1 February 2012
Available online 9 February 2012

## Abstract

The dielectric properties of Cr + La co-doped $CaCu_3Ti_4O_{12}$ ceramics prepared by a solid-state reaction method were evaluated and compared to Cr-doped, La-doped, and parent $CaCu_3Ti_4O_{12}$ (CCTO). Their structure and grain size were evaluated by X-ray diffraction and scanning electron microscopy, respectively. No secondary phase was detected based on the XRD analysis. The results show that, the room temperature dielectric loss of the co-doped samples is reduced to 43% compared to CCTO and their dielectric permittivity is higher than the un-doped, Cr-doped, and La-doped samples at frequencies over 325 kHz, 30 kHz, and 12 Hz, respectively. Furthermore, the temperature stability of the co-doped sample is significantly more convenient than that of CCTO, and its dielectric loss is three times lower. The results also indicated that the co-doping method is effective in reducing the dielectric loss, still maintaining the high dielectric permittivity.

*Keywords:* A. Powders: solid state reaction; C. Dielectric properties; D. Perovskites

## 1. Introduction

In the last decade, electroceramics associated with colossal dielectric constants (CDC) have been on increasing demand due to their possible technological applications [1–3]. The advantage of high dielectric permittivity ($\varepsilon_r$) substances is the fact that they allow a reduction in the physical volume of capacitive components and thereby a decrease in the size of device products [4]. $CaCu_3Ti_4O_{12}$ (CCTO) has recently attracted much research interest because of its extraordinarily high dielectric constant ($\varepsilon_r$) of $10^4$ at room temperature [5–7]. Although the CCTO ceramics has a considerably high value of dielectric permittivity in a wide range of temperature and frequency [5–17], making it an utilizable material for practical applications in microelectronics such as capacitors and memory devices [11–13], their relatively high dissipation factor (tan $\delta$) restricts their applications [11,14,18,19]. However, to modify the dielectric loss, it is necessary to know the mechanism of giant dielectric response in these materials [14]. Although there has been substantial debate about the origin of the unusual CCTO dielectric property [9], the internal barrier layer capacitance effects are supposed to have the main contributions to the dielectric response in the CCTO ceramics [20–24]. Recently, many researchers have focused on decreasing tan $\delta$ and, to date some successful routes including doping, substituting and two-phase composites have been reported [6,7,11,14,18,19]; however, the effect of Cr + La co-doping on the dielectric properties of CCTO has not been investigated.

In this work, the dielectric properties of La + Cr co-doped CCTO prepared by a solid state reaction method were investigated and compared with results obtained for the samples un-doped and doped by Cr and La separately. The main aim of this work is the reduction of the dielectric loss of CCTO in a wide range of frequency without any deterioration effect on its dielectric permittivity.

## 2. Experimental procedure

Un-doped CCTO, $CaCu_3Ti_{3.9}Cr_{0.133}O_{12}$ (CCTCO), $La_{0.033}Ca_{0.95}Cu_3Ti_4O_{12}$ (LCCTO) and co-doped $La_{0.033}Ca_{0.95}Cu_3Ti_{0.9}Cr_{0.133}O_{12}$ (LCCTCO) powders were prepared by a solid state reaction method. The stoichiometric amounts of highly pure $CaCO_3$ (99.5%), CuO (99.5%), $TiO_2$ (99.99%), $La_2O_3$ and $Cr_2O_3$ (99.9%) were mixed and milled using a

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* Corresponding author. Tel.: +98 711 7354500; fax: +98 711 7354520.
*E-mail address:* Alizadeh@sutech.ac.ir (M. Alizadeh).

doi:10.1016/j.ceramint.2012.02.005

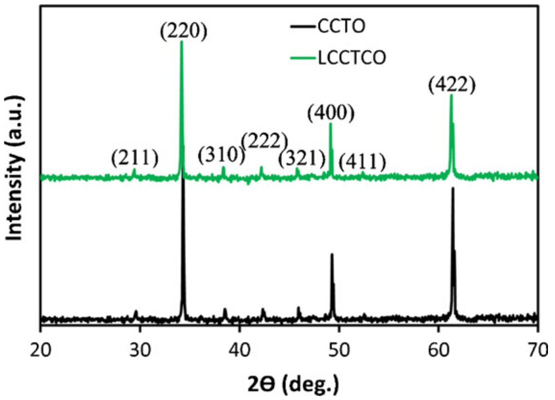

Fig. 1. XRD pattern of CCTO and LCCTCO sintered at 1100 °C for 8 h.

planetary laboratory ball-mill (Sepahan, 84D) for 2 h in ethanol. Subsequently, these mixtures were oven dried for 2 h followed by furnace calcination in an alumina crucible at 900 °C for 12 h under air. The calcinated powders were then pressed into pellets (8 mm in diameter and 1.2 mm in thickness) with a uniaxial pressure of 200 MPa after sufficient grounding. The pressed pellets were sintered in air at 1100 °C for 8 h. The XRD patterns of the sintered samples were obtained at room temperature, in an XRD, Bruker Advance 2 system, with Kα radiation at 40 kV and 40 mA. The microstructural features and grain size distribution in the sintered pellets were studied by a scanning electron microscope (SEM, JEOL-JSM 6340F). For electrical characterizations, the sintered disk pellets were surface-polished and then coated with silver paint and fired at 575 °C for 20 min; finally, dielectric spectroscopy measurements were carried out by a frequency response analyzer (HP 4284A LCR meter) in the frequency range of 12 Hz to 1 MHz.

## 3. Results and discussion

Fig. 1 illustrates the XRD patterns of the pellets sintered at 1100 °C for 8 h. The peaks are identified to belong to CCTO which overlap with the perovskite structure peaks according to JCPDS-05-0566. No secondary phase containing La and Cr was detected, probably because their quantities are lower than the detection limits of the technique.

The SEM images of the fractured surface of the un-doped and co-doped CCTO ceramics sintered at 1100 °C for 8 h are illustrated in Fig. 2. The CCTO sample displays a wide range of the grain size distribution (10-80 μm), where its microstructure consists of some grains showing abnormal grain growth (due to the creation of a liquid phase during the sintering process) and smaller grains occupying intermittent regions (Fig. 2(a)). On the other hand, in the co-doped samples (Fig. 2(b)) the grain size is reduced remarkably to about 8 μm and no evidence of abnormal grain growth is observable. Note that energy-dispersive X-ray spectroscopy assessments (not shown) indicated that although CCTO grain boundaries consist of a Cu-enriched phase, in the LCCTCO sample owing to the existence of the Cr and La dopants the Cu segregation at grain boundaries is prevented.

Fig. 3 demonstrates the room-temperature dielectric permittivity and dielectric loss for the CCTO, LCCTO, CCTCO, and LCCTCO samples sintered at 1100 °C for 8 h. As shown in Fig. 3, all the samples except LCCTO exhibit large $\varepsilon_r$ values (>8000) at the frequency of 120 Hz. The LCCTO ceramic shows the lowest $\varepsilon_r$ value of about 1110 and CCTO exhibits the highest $\varepsilon_r$ value of about $2 \times 10^4$, while the others indicate intermediate $\varepsilon_r$ values. By increasing the frequency to 1 kHz, the dielectric permittivity of all the samples decreased, albeit the major decrease in the dielectric constant was observed for the CCTO and CCTCO samples. It has been reported that the high $\varepsilon_r$ values at low frequencies originate from the interfacial polarization of the sample/electrode surface contact [6,7,15]. CCTO displays a Debye-type relaxation at about 100 kHz, arising from the interfacial polarization between grains and grain boundaries [5–7,15], although this relaxation occurs for the co-doped sample at frequencies about one order of magnitude higher. As it can be seen, due to an abrupt degradation in the permittivity of CCTO and CCTCO by increasing the frequency, the co-doped sample possesses higher $\varepsilon_r$ than those at frequencies over 325 kHz and 30 kHz, respectively. The increase in frequency to 1 MHz causes large differences among $\varepsilon_r$ of these samples, where $\varepsilon_r$ of CCTO, CCTCO, and LCCTCO is 2013, 829, and 3074, respectively.

As it is observed in Fig. 3, the overall appearance of the tan $\delta$ curves for the samples, except LCCTO, is similar, while the tan $\delta$ values are different significantly. At low frequencies, the dielectric loss is high and with increasing the frequency tan $\delta$ decreases and reaches lowest values and is enhanced again by increasing the frequency values. It can be worth mentioning that the tan $\delta$ of the co-doped sample at a wide frequency range is lower than the parent CCTO sample. For instance, tan $\delta$ of the co-doped and un-doped samples at 10 kHz is 0.137 and 0.141,

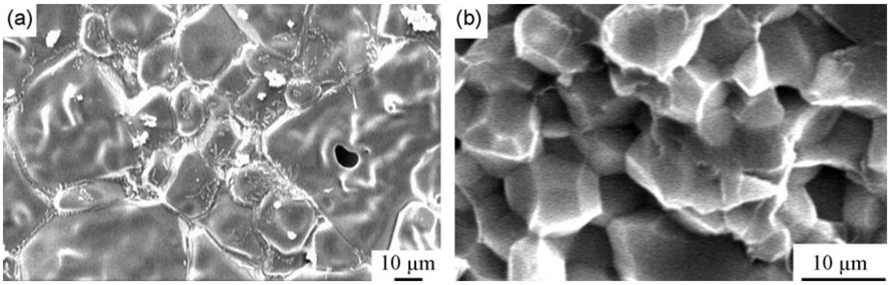

Fig. 2. SEM micrograph of (a) CCTO and (b) LCCTCO sintered at 1100 °C for 8 h.

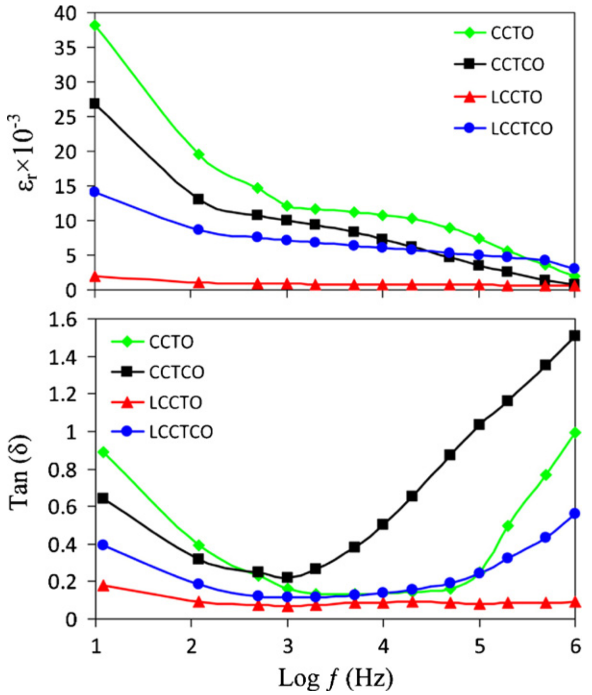

Fig. 3. Variation of the dielectric permittivity (a) and dielectric loss (b) of the samples with frequency at ambient temperature.

at 100 kHz is 0.243 and 0.251, and at 1 MHz is 0.563 and 0.991, respectively. As it can be seen, co-doping can reduce tan $\delta$ to 43% compared to CCTO.

The dielectric properties of all the samples versus temperature at 10 kHz are depicted in Fig. 4. The dielectric constant and dissipation factor of all the samples increased continuously by increasing temperature, although the rate of these enhancements was not the same. These observations are in accordance with reports of Mu et al. [15] and Yu et al. [14]. Concerning Fig. 4, it can be seen that the thermal stability of LCCTO and subsequently LCCTCO is considerably higher than that of CCTO and CCTCO; however, since the dielectric permittivity of the co-doped sample (LCCTCO) is noticeably higher than that of LCCTO, it can be implied that the optimal dielectric property can be achieved by co-doping. The dielectric loss of CCTO, CCTCO, LCCTCO, and LCCTO at 25 °C is 0.13, 0.502, 0.128, and 0.083, respectively. These tan $\delta$ values reach 0.793, 1.36, 0.216, and 0.111 as temperature increases to 150 °C. Thus, the loss factor of the co-doped sample is three times lower than CCTO at 150 °C.

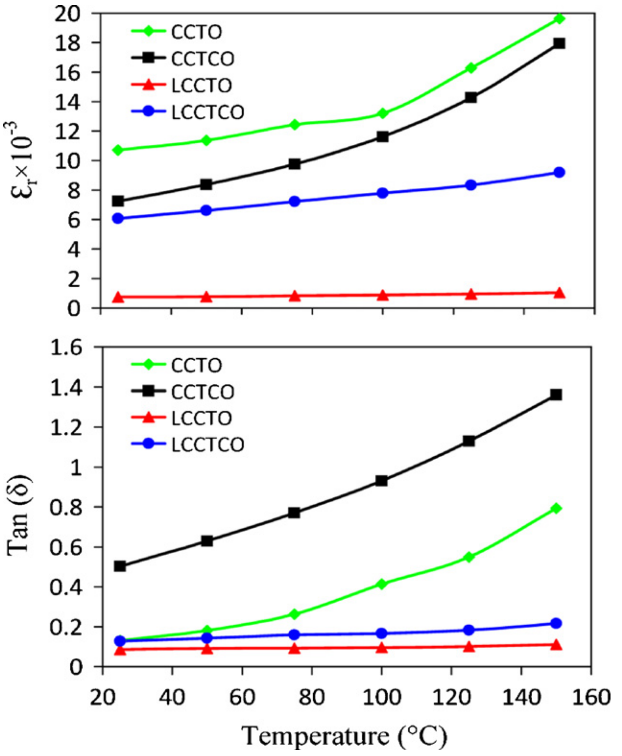

Fig. 4. Dielectric permittivity of samples as a function of temperature at the frequency of 10 kHz.

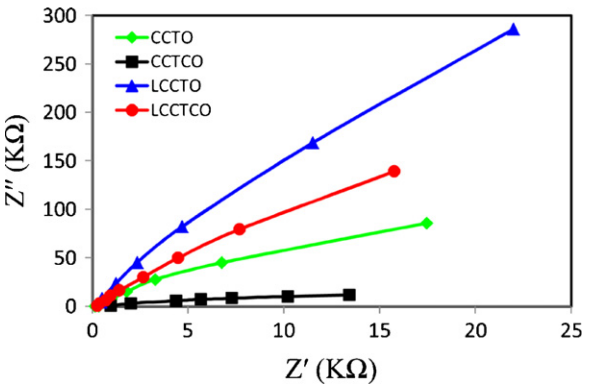

Fig. 5. Complex impedance plots of the prepared ceramics.

In order to recognize the effect of grain and grain boundaries resistance on the dielectric properties, the complex impedance plot at room temperature is provided in Fig. 5. All the samples indicate a single semicircular arc with a non-zero intercept on the $Z'$-axis at high frequencies, whereas the diameter corresponding to the grain boundary resistance increases with Cr + La co-doping. The impedance spectrum data show that the system can be modeled by the IBLC equivalent circuit consisting of two parallel RC elements connected in series, where the capacitance $C_g$ and the resistance $R_g$ describe the grain effects, and capacitance $C_{gb}$ and the resistance $R_{gb}$ represent the high resistance grain boundary regions. By concerning the model, a considerable decrease in the grain boundary resistance and a significant increase in the grain resistance lead to the loss of polarization. On the other hand, the presence of high resistance grain boundaries and semiconducting grains at the model is important to achieve superior dielectric properties. It can be concluded that the giant dielectric permittivity of the CCTO system at low-to-medium frequencies (from 1 kHz to 1 MHz) originates from interfacial polarization at grain boundaries. It can be concluded that the giant dielectric permittivity of the CCTO system at low-to-medium frequencies (from 1 kHz to 1 MHz) originates from interfacial polarization at grain boundaries. Based on the brickwork layer model (BLM) suggested by Adams et al. [2,3], the higher dielectric permittivity of CCTO compared to LCCTCO originates from its big grains, where the bigger grains give higher $\varepsilon_r$ values. However, owing to the decrease in the grain boundary resistance of the ceramics especially CCTCO and CCTO, their dielectric properties are degraded at high frequencies. In the case of LCCTCO and especially LCCTO, the more stability of grain boundary resistance (due to smaller grains and consequently the greater number of grain boundaries [16,17]) at the broad range of frequencies is responsible for low tan $\delta$.

Based on the aforementioned results, it can be seen that the dielectric permittivity of the co-doped ceramics is more convenient than La-doped CCTO. In addition, the dielectric constant of the co-doped sample is more than that of CCTO and CCTCO at frequencies over 325 kHz and 30 kHz, respectively. Moreover, because of the more grain boundary resistance of co-doped CCTO, its dielectric loss is considerably lower than the un-doped and Cr-doped CCTO samples at a wide range of frequency. Consequently, it can be implied that the co-doped method is an efficient route to improve the dielectric properties of the CCTO ceramics with a proper dielectric permittivity and low dielectric loss.

## 4. Conclusions

The conclusions drawn from the results can be summarized as follows:

(1) The dielectric permittivity of Cr + La co-doped CCTO is higher than that of the un-doped, Cr-doped, and La-doped samples at frequencies over 325 kHz, 30 kHz, and 12 Hz, respectively.
(2) The dielectric loss of co-doped CCTO is considerably lower than the un-doped and Cr-doped CCTO samples at a wide range of frequency.
(3) LCCTCO is more thermal stable than CCTO and its dielectric loss is three times lower than CCTO at 150 °C.
(4) The Cr + La co-doping method is an efficient method to improve the dielectric properties of the CCTO ceramics with a proper dielectric permittivity and low dielectric loss.

## References

[1] C.C. Homes, T. Vogt, S.M. Shapiro, S. Wakimoto, A.P. Ramirez, Optical response of high-dielectric-constant perovskite-related oxide, Science 293 (5530) (2001) 673–676.

[2] D.C. Sinclair, T.B. Adams, F.D. Morrison, A.R. West, $CaCu_3Ti_4O_{12}$: one-step internal barrier layer capacitor, Appl. Phys. Lett. 80 (12) (2002) 2153–2155.

[3] T.B. Adams, D.C. Sinclair, A.R. West, Giant barrier layer capacitance effects in $CaCu_3Ti_4O_{12}$ ceramics, Adv. Mater. 14 (18) (2002) 1321–1323.

[4] B. Renner, P. Lunkenheimer, M. Schetter, A. Loidl, A. Reller, S.G. Ebbinghaus, Dielectric behavior of copper tantalum oxide, J. Appl. Phys. 96 (8) (2004) 4400–4404.

[5] T.T. Fang, H.K. Shiau, Mechanism for developing the boundary barrier layers of $CaCu_3Ti_4O_{12}$, J. Am. Ceram. Soc. 87 (11) (2004) 2072–2079.

[6] B.S. Prakash, K.B.R. Varma, Influence of sintering conditions and doping on the dielectric relaxation originating from the surface layer effects in $CaCu_3Ti_4O_{12}$ ceramics, J. Phys. Chem. Solids 68 (2007) 490–502.

[7] B.S. Prakash, K.B.R. Varma, Effect of sintering conditions on the dielectric properties of $Cu_3Ti_4O_{12}$ and $La_{2/3}Cu_3Ti_4O_{12}$ ceramics: a comparative study, Physica B 382 (2006) 312–319.

[8] L. Wu, Y. Zhu, S. Park, S. Shapiro, G. Shirane, Defect structure of the high-dielectric-constant perovskite $CaCu_3Ti_4O_{12}$, Phys. Rev. B 71 (2005) 014118.

[9] M.A. Subramanian, D. Li, N. Duan, B.A. Reisner, A.W. Sleight, High dielectric constant in $ACu_3Ti_4O_{12}$ and $ACu_3Ti_3FeO_{12}$ phases, J. Solid State Chem. 151 (2) (2000) 323–325.

[10] A.P. Ramirez, M.A. Subramanian, M. Gardel, G. Blumberg, D. Li, T. Vogt, S.M Shapiro, Giant dielectric constant response in a copper–titanate, Solid State Commun. 115 (2000) 217–220.

[11] S. Jin, H. Xia, Y. Zhang, Effect of La-doping on the properties of $CaCu_3Ti_4O_{12}$ dielectric ceramics, Ceram. Int. 35 (2009) 309–313.

[12] S.W. Choi, S.H. Hong, Effect of Al doping on the electric and dielectric properties of $CaCu_3Ti_4O_{12}$, J. Am. Ceram. Soc. 90 (12) (2007) 4009–4011.

[13] D.L. Sun, A.Y. Wu, S.T. Yin, Structure, properties, and impedance spectroscopy of $CaCu_3Ti_4O_{12}$ ceramics prepared by sol–gel process, J. Am. Ceram. Soc. 91 (1) (2008) 169–173.

[14] H. Yu, H. Liu, H. Hao, D. Luo, M. Cao, Dielectric properties of $CaCu_3Ti_4O_{12}$ ceramics modified by $SrTiO_3$, Mater. Lett. 62 (2008) 1353–1355.

[15] C. Mu, H. Zhang, Y. He, P. Liu, Influence of temperature on dielectric properties of Fe-doped $CaCu_3Ti_4O_{12}$ ceramics, Physica B 405 (2010) 386–389.

[16] P.R. Bueno, R. Tararan, R. Parra, E. Joanni, M.A. Ramirez, W.C. Ribeiro, E. Longo, J.A. Varela, A 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. 42 (2009) 055404.

[17] T. Li, Z. Chen, F. Chang, J. Hao, J. Zhang, The effect of $Eu_2O_3$ doping on $CaCu_3Ti_4O_{12}$ varistor properties, J. Alloys Compd. 484 (2009) 718–722.

[18] W. Kobayashi, I. Terasaki, $CaCu_3Ti_4O_{12}/CaTiO_3$ composite dielectrics: Ba/Pb-free dielectric ceramics with high dielectric constants, J. Appl. Phys. 87 (2005) 032902.

[19] E.A. Patterson, S. Kwon, C.C. Huang, D.P. Cann, Effects of $ZrO_2$ additions on the dielectric properties of $CaCu_3Ti_4O_{12}$, J. Appl. Phys. 87 (2005) 182911.

[20] L. Zhang, Z.J. Tang, Polaron relaxation and variable-range-hopping conductivity in the giant-dielectric-constant material $CaCu_3Ti_4O_{12}$, Phys. Rev. B 70 (17) (2004) 174306.

[21] S.Y. Chung, I.D. Kim, S.J.L. Kang, Strong nonlinear current–voltage behaviour in perovskite-derivative calcium copper titanate, Nat. Mater. 3 (11) (2004) 774–778.

[22] M.J. Pan, B.A. Bender, A bimodal grain size model for predicting the dielectric constant of calcium copper titanate ceramics, J. Am. Ceram. Soc. 88 (9) (2005) 2611–2614.

[23] S.H. Hong, D.Y. Kim, H.M. Park, Y.M. Kim, Electric and dielectric properties of Nb-doped $CaCu_3Ti_4O_{12}$ ceramics, J. Am. Ceram. Soc. 90 (7) (2007) 2118–2121.

[24] P. Jha, P. Arora, A.K. Ganguli, Polymeric citrate precursor route to the synthesis of the high dielectric constant oxide $CaCu_3Ti_4O_{12}$, Mater. Lett. 57 (2003) 2443–2446.