NANO EXPRESS

Open Access

Dramatically enhanced non-Ohmic properties and maximum stored energy density in ceramic-metal nanocomposites: CaCu₃Ti₄O₁₂/Au nanoparticles

Wattana Tuichai¹, Saowalak Somjid¹, Bundit Putasaeng², Teerapon Yamwong², Apiwat Chompoosor^{3,4*}, Prasit Thongbai^{3,4*}, Vittaya Amornkitbamrung^{3,4} and Santi Maensiri⁵

Abstract

Non-Ohmic and dielectric properties of a novel CaCu₃Ti₄O₁₂/Au nanocomposite were investigated. Introduction of 2.5 vol.% Au nanoparticles in CaCu₃Ti₄O₁₂ ceramics significantly reduced the loss tangent while its dielectric permittivity remained unchanged. The non-Ohmic properties of CaCu₃Ti₄O₁₂/Au (2.5 vol.%) were dramatically improved. A nonlinear coefficient of \approx 17.7 and breakdown electric field strength of 1.25 × 10⁴ V/m were observed. The maximum stored energy density was found to be 25.8 kJ/m³, which is higher than that of pure CaCu₃Ti₄O₁₂ by a factor of 8. Au addition at higher concentrations resulted in degradation of dielectric and non-Ohmic properties, which is described well by percolation theory.

Keywords: Nanocomposite; Dielectric permittivity; Percolation threshold; Varistor

Background

Ceramic materials with high dielectric permittivity (ϵ') have been intensively studied because of their potential for multilayer ceramic capacitor applications. The dielectric materials used in these devices must exhibit a high ε' with very low loss tangent (tan δ). They also need to have a high breakdown voltage to support high-energy density storage applications. The energy density (U) performance of capacitors can be expressed as $U = \varepsilon \epsilon_0 E_b^2/2$, where $E_{\rm b}$ is electric field breakdown strength [1]. Recently, dielectric ceramics homogeneously filled with metallic particles have been of considerable scientific and technological interest. This is due to their greatly enhanced dielectric response as well as an improved tunability of ϵ' [2-11]. Generally, ϵ' increases rapidly in the region of the percolation threshold (PT) [4,9]. For the Ag-Ba_{0.75}Sr_{0.25}TiO₃ composite [9], the large increase in ε' was suggested to result from the percolation effect. Improved tunability of Ba_{0.75}Sr_{0.25}TiO₃ ceramics

* Correspondence: apiwat@kku.ac.th; pthongbai@kku.ac.th

Full list of author information is available at the end of the article



was hypothesized to be the effect of either large induced internal electric fields within the thin $Ba_{0.75}Sr_{0.25}TiO_3$ layer sandwiched by electrode-like metallic Ag particles or improved densification of ceramic composites. However, E_b of a metal-ceramic composite abruptly decreased as the metallic filler concentration increased to PT [4].

CaCu₃Ti₄O₁₂ (CCTO) is one of the most interesting ceramics because it has high ε' values. CCTO polycrystalline ceramics can also exhibit non-Ohmic properties [12-20]. These two properties give CCTO potential for applications in capacitor and varistor devices, respectively. Unfortunately, high tan δ (>0.05) of CCTO ceramics is still one of the most serious problems preventing its use in applications [10,12,17]. The application of CCTO ceramics in varistor devices was limited by their low nonlinear coefficient (α) and $E_{\rm b}$ values. For energy storage devices, both ε' and $E_{\rm b}$ need to be enhanced in order to make high performance energy-density capacitors. Therefore, investigations to systematically improve CCTO ceramics properties are very important.

Methods

In this work, $CaCu_3Ti_4O_{12}$ powder was prepared by a solid state reaction method. First, $CaCO_3$, CuO, and TiO_2 were mixed homogeneously in ethanol for 24 h

© 2013 Tuichai et al.; licensee Springer. This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/2.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

³Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

⁴Nanotec-KKU Center of Excellence on Advanced Nanomaterials for Energy Production and Storage, Khon Kaen 40002, Thailand

using ZrO₂ balls. Second, the resulting mixture was dried and then ground into fine powders. Then, dried powder samples were calcined at 900°C for 6 h. HAuCl₄, sodium citrate, and deionized water were used to prepare Au NPs by the Turkevich method [21]. CCTO/Au nano-composites with different Au volume fractions of 0, 0.025, 0.05, 0.1, and 0.2 (abbreviated as CCTO, CCTO/Au1, CCTO/Au2, CCTO/Au3, and CCTO/Au4 samples, respectively) were prepared. CCTO and Au NPs were mixed and pressed into pellets. Finally, the pellets were sintered in air at 1,060°C for 3 h.

X-ray diffraction (XRD; Philips PW3040, Philips, Eindhoven, The Netherlands) was used to characterize the phase formation of sintered CCTO/Au nanocomposites. Scanning electron microscopy (SEM; LEO 1450VP, LEO Electron Microscopy Ltd, Cambridge, UK) coupled with energy-dispersive X-ray spectrometry (EDS) were used to characterize the microstructure of these materials. Transmission electron microscopy (TEM) (FEI Tecnai G^2 , FEI, Hillsboro, OR, USA) was used to reveal Au NPs. The polished surfaces of sintered CCTO/Au samples were coated with Au sputtered electrode. Dielectric properties were measured using an Agilent 4294A Precision Impedance Analyzer (Agilent Technologies, Santa Clara, CA, USA) over the frequency range from 10^2 to 10^7 Hz with an oscillation voltage of 0.5 V.

Results and discussion

Figure 1 shows the XRD patterns of the CCTO/Au nanocomposites, confirming the major CCTO matrix phase (JCPDS 75–2188) and the minor phase of Au filler (JCPDS 04–0784). An impurity phase of CaTiO₃ (CTO) was also observed in the XRD patterns of the CCTO/Au samples. The intensity ratio between the (111) peak of Au and the (200) peak of CCTO was found to increase



with increasing Au concentrations. Lattice parameters of the CCTO phase for the CCTO, CCTO/Au1, CCTO/ Au2, CCTO/Au3, and CCTO/Au4 samples were calculated to be 7.391, 7.391, 7.391, 7.390, and 7.390 Å, respectively. These parameters are nearly the same in value and are comparable to those reported in the literature [12,16,17]. This means that Au was not substituted into any sites in the CCTO lattice.

The distribution of the Au filler in the microstructure of CCTO matrix is revealed in Figure 2a,b,c,d. The inset of Figure 2a shows the TEM image of Au NPs with particle sizes of about 50 to 100 nm. Two distinct phases were observed, consisting of regular grains and light particles appearing as spots, which are indicated by arrows. The amount and particle size of the lighter phase increased with increasing Au NP concentrations. Figure 2e,f shows the EDS spectra of the CCTO/Au1 sample at the location of a light particle (inset of panel e) and a regular grain (inset of panel f), respectively. It is important to mention that before the SEM and EDS techniques were performed, surfaces of all the CCTO/Au samples were not coated with Au sputtered layer in order to identify the Au NPs in the CCTO matrix. Therefore, the light particles are clearly indicated as Au phase. Most of Au particles are located at the grain boundary (GB) or at the triple point junction between grains.

In Figure 3, ε' values at 1 kHz and RT for the CCTO, CCTO/Au1, CCTO/Au2, CCTO/Au3, and CCTO/Au4 samples were found to be 3,864, 3,720, 4,293, 5,039, and 20,060, respectively. Their tanð values were 0.115, 0.058, 0.087, 0.111, and 0.300, respectively (inset (2)). The low-frequency ε' and tanð of the CCTO, CCTO/Au1, CCTO/Au2, and CCTO/Au3 samples were slightly different (inset (1)). Both ε' and tanð were strongly enhanced as the concentration of Au NP filler was increased to 20 vol.%. Generally, dramatic changes in metal-insulator matrix composites in the critical region are attributed to the percolation effect [4,7,9,17,22-24]. A rapid increase in effective dielectric constant (ε'_{eff}) of the composites can be described by the power law [4,9,22,24]:

$$\varepsilon_{\rm eff}' = \varepsilon_{\rm matrix}' \left| \frac{f_{\rm c} - f}{f_{\rm c}} \right|^{-q}, \tag{1}$$

where ε'_{matrix} is the dielectric constant of the insulator matrix, f_c is the PT, f is the volume fraction of conductive filler, and q is a critical component. As shown in Figure 3, the dependence of ε' on the volume fraction of Au NPs can be well described by Eq. (1). From the fitted result, f_c and q were found to be 0.21 and 0.55, respectively. In the case where conductive fillers were in spherical form, the PT of the two-phase random composite was theoretically calculated to be 0.16 [22,24]. f_c of the CCTO/Au system was larger than the calculated value (0.16). However, the



critical exponent ($q \approx 0.55$) was lower than the lower limit of the normal range ($q \approx 0.8$ to 1), indicating a slow increase in ε' with increasing metal content. Deviation of f_{c} and q from percolation theory may be due to the agglomeration of Au NPs to form large Au particles in the CCTO matrix, as clearly seen in Figure 2d. f_c of the CCTO/Au system is comparable to those observed in the Ba_{0.75}Sr_{0.25-} TiO_3/Ag ($f_c = 0.285$) [9] and $BaTiO_3/Ni$ ($f_c = 0.232$ to 0.310) [4,7] microcomposite systems. In the cases of the nanocomposite systems of PbTiO₃/Ag [8] and Pb_{0.4}Sr_{0.6}TiO₃/ Ag [11], f_c values were found to be 0.16. Actually, the obtained $f_{\rm c}$ and q might not be highly accurate values or not the best values due to a large range of Au NPs volume fraction between 0.1 and 0.2. However, one of the most important factors for the observed higher f_c for the CCTO/Au system clearly suggested a morphology transition from nanocomposite to microcomposite as Au NP concentration was increased to 20 vol.%. This result is consistent to the microcomposite systems of Ba_{0.75}Sr_{0.25}TiO₃/Ag [9] and BaTiO₃/Ni [4,7]. Generally, the distribution of fillers in a matrix has an influence on the value of f_c . For spherical fillers, f_c of randomly distributed fillers is given by the ratio between the particle size of the matrix phase (R_1) and the filler (R_2) [22]. When $R_1/R_2 \approx 1$ or $R_1 \approx R_2$, we ob $tain f_c \approx 0.16$. As $R_1/R_2 > 1$ or $R_1 > > R_2$, the fillers fill the interstitial space between the matrix phase particles, resulting in a continuous percolating cluster of the filler at $f_{\rm c}$ < 0.16. As shown in Figure 2, the particle size of CCTO (R_1) is larger than that of Au NPs (R_2) , i.e., $R_1/R_2 >> 1$. Theoretically, f_c of the CCTO/Au NP system should be lower than 0.16. However, the observed f_c value in the CCTO/Au system was found to be 0.21. Therefore, it is



strongly indicated that the primary factor that has a great effect on f_c is the agglomeration of the Au filler.

Large increases in ε' of percolating composites are generally attributed to formation of microcapacitor networks in the composites and/or Maxwell-Wagner polarization [4,9,22]. For pure CCTO ceramics, the giant dielectric response is normally associated with the mean grain size [16,17,25]. Although there is a small amount of relatively large grains (5 to 10 µm) in the microstructure of CCTO/Au3 and CCTO/Au4 (data not presented), the large observed enhancement of ε' is likely due to the percolation effect.

According to the effective medium theory [26], the average microscopic electric field inside the ceramic matrix filled with conductive particles increases in the region of the PT, which results in a significant decrease in $E_{\rm b}$. Figure 4 shows the non-Ohmic properties of the CCTO/Au nanocomposites as a plot of electrical current density (J) vs. electric field strength (E). α values of the CCTO, CCTO/Au1, CCTO/Au2, CCTO/Au3, and CCTO/Au4 samples were calculated in the range of J = 1to 10 mA/cm² and found to be 7.38, 17.67, 11.08, 5.05, and 3.08, respectively. $E_{\rm b}$ values (obtained at $J = 1 \text{ mA/cm}^2$) were found to be 4.26×10^3 , 1.25×10^4 , 1.17×10^4 , 2.50×10^3 , and 7.84×10^2 V/cm, respectively. α and $E_{\rm b}$ initially showed a strong increase with introduction of 2.5 to 5.0 vol.% of Au NPs into CCTO (inset of Figure 4). Both parameters greatly decreased with further increasing Au NPs from 10 to 20 vol.%, which is due to the percolation effect [4]. In the region of the PT, electrical conduction in composites increased dramatically, resulting in a large decrease in $E_{\rm b}$. This observation is consistent with the effective medium theory [26]. Therefore, it is reasonable to suggest that the increases in ε' and tan δ observed



in the CCTO/Au4 sample were mainly attributed to the percolation effect; while, the effect of grain size effect is slight.

The CCTO/Au1 sample exhibited the best non-Ohmic properties among all samples. These values are comparable to those observed in CaCu₃Ti_{3.8}Sn_{0.2}O₁₂ ceramic [27]. There are many factors that are potentially responsible for strong improvement of non-Ohmic properties. It was found that the non-Ohmic properties of CCTO ceramics could effectively be improved by fabricating composite systems of CCTO/CTO [28,29]. As shown in Figure 1, the observed CTO phase in all of the CCTO/Au composites tended to increase with increasing Au content. However, the non-Ohmic properties of CCTO/Au strongly degraded as the Au filler concentration increased. Thus, the excellent non-Ohmic properties of the CCTO/Au1 sample are not mainly caused by a CTO phase. For CCTO polycrystalline ceramics, the non-Ohmic behavior is due to the existence of Schottky barriers at the GBs [13]. Thus, the existence of metallic Au NPs at the GBs of CCTO ceramics may contribute the formation of Schottky barriers at GBs. However, the mechanism by which Au NPs contribute to enhancement of non-Ohmic properties is still unclear.

It is worth noting that improved nonlinear properties of the CCTO/Au1 sample may also be related to modification of microstructure. Although the introduction of metallic particles in a ceramic matrix with concentration near the PT can dramatically enhance the dielectric response, a large increase in the conduction of charge carriers was observed simultaneously, leading to decreases in E_b and energy density. The maximum stored energy densities of all the samples were calculated and found to be 3.11, 25.8, 26.0, 1.39, and 0.54 kJ/m³ for the CCTO, CCTO/Au1, CCTO/Au2, CCTO/Au3, and CCTO/Au4 samples, respectively. Notably, introduction of Au NPs into CCTO ceramics in small concentrations, between 2.5 and 5.0 vol.%, caused a strong increase in the maximum stored energy density as well as their non-Ohmic properties.

Conclusions

In conclusion, the investigation of non-Ohmic and dielectric properties of CCTO/Au revealed that addition of Au NPs to CCTO in the concentration of 2.5 vol.% can decrease tan δ , while ε' was unaltered. The non-Ohmic properties of this composition were also successfully improved showing $\alpha \approx 17.7$ and $E_b \approx 1.25 \times 10^4$ V/cm. The maximum stored energy density of CCTO ceramics were significantly enhanced by introducing of Au NPs in concentrations of 2.5 to 5.0 vol.%. The dielectric and non-Ohmic properties as well as energy density were degraded when Au NP concentrations were greater. The mechanisms of dielectric response and non-Ohmic properties can be well described by using the percolation theory.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

WT carried out all the experiments, except for the preparation of Au nanoparticles. SS prepared Au nanoparticles. BP and TY offered technical support for the dielectric and I-V measurements. AC and PT supervised the research, designed the experiments, and participated in preparing the draft of the manuscript. PT revised the manuscript. VA and SM gave suggestions on the study. All authors read and approved the final manuscript.

Acknowledgements

This work was financially supported by the Nanotechnology Center (NANOTEC), NSTDA, Ministry of Science and Technology, Thailand, through its program of Center of Excellence Network. WT extends his gratitude to the Thailand Graduate Institute of Science and Technology (TGIST) for his Master of Science Degree scholarship.

Author details

¹Materials Science and Nanotechnology Program, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand. ²National Metal and Materials Technology Center (MTEC), Thailand Science Park, Pathumthani 12120, Thailand. ³Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand. ⁴Nanotec-KKU Center of Excellence on Advanced Nanomaterials for Energy Production and Storage, Khon Kaen 40002, Thailand. ⁵School of Physics, Institute of Science, Suranaree University, Nakhon Ratchasima 30000, Thailand.

Received: 3 October 2013 Accepted: 16 November 2013 Published: 21 November 2013

References

- Song Y, Shen Y, Hu P, Lin Y, Li M, Nan CW: Significant enhancement in energy density of polymer composites induced by dopamine-modified Ba0.6Sr0.4TiO3 nanofibers. *Appl Phys Lett* 2012, 101:152904.
- Halder N, Sharma AD, Khan SK, Sen A, Maiti HS: Effect of silver addition on the dielectric properties of barium titanate based low temperature processed capacitors. *Mater Res Bull* 1999, 34:545.
- Duan N, ten Elshof JE, Verweij H, Greuel G, Dannapple O: Enhancement of dielectric and ferroelectric properties by addition of Pt particles to a lead zirconate titanate matrix. *Appl Phys Lett* 2000, 77:3263.
- Pecharromán C, Esteban-Betegón F, Bartolomé JF, López-Esteban S, Moya JS: New percolative BaTiO₃–Ni composites with a high and

frequency-independent dielectric constant ($\epsilon_r \approx 80000$). Adv Mater (Weinheim, Ger) 2001, 13:1541.

- Chen R, Wang X, Gui Z, Li L: Effect of silver addition on the dielectric properties of barium titanate-based X7R ceramics. J Am Ceram Soc 2003, 86:1022.
- Jayadevan KP, Liu CY, Tseng TY: Dielectric characteristics of nanocrystalline Ag–Ba0.5Sr0.5TiO3 composite thin films. *Appl Phys Lett* 2004, 85:1211.
- Chen Z, Huang J, Chen Q, Song C, Han G, Weng W, Du P: A percolative ferroelectric–metal composite with hybrid dielectric dependence. Scr Mater 2007, 57:921.
- Wang Z, Hu T, Tang L, Ma N, Song C, Han G, Weng W, Du P: Ag nanoparticle dispersed PbTiO₃ percolative composite thin film with high permittivity. *Appl Phys Lett* 2008, 93:222901.
- Huang J, Cao Y, Hong M, Du P: Ag-Ba0.75Sr0.25TiO3 composites with excellent dielectric properties. *Appl Phys Lett* 2008, 92:022911.
- Chen C, Wang C, Ning T, Lu H, Zhou Y, Ming H, Wang P, Zhang D, Yang G: Enhanced nonlinear current–voltage behavior in Au nanoparticle dispersed CaCu₃Ti₄O₁₂ composite films. *Solid State Commun* 2011, 151:1336.
- 11. Wang Z, Hu T, Li X, Han G, Weng W, Ma N, Du P: Nano conductive particle dispersed percolative thin film ceramics with high permittivity and high tunability. *Appl Phys Lett* 2012, **100**:132909.
- Subramanian MA, Li D, Duan N, Reisner BA, Sleight AW: High dielectric constant in ACu₃Ti₄O₁₂ and ACu₃Ti₃FeO₁₂ phases. J Solid State Chem 2000, 151:323.
- Chung S-Y, Kim I-D, Kang S-JL: Strong nonlinear current–voltage behaviour in perovskite-derivative calcium copper titanate. *Nat Mater* 2004, 3:774.
- Li J-y, Xu T-w, Li S-t, Jin H-y, Li W: Structure and electrical response of CaCu₃Ti₄O₁₂ ceramics: effect of heat treatments at the high vacuum. *J Alloys Compd* 2010, 506:L1.
- Li J, Jia R, Tang X, Zhao X, Li S: Enhanced electric breakdown field of CaCu₃Ti₄O₁₂ceramics: tuning of grain boundary by a secondary phase. *J Phys D Appl Phys* 2013, 46:325304.
- Thongbai P, Jumpatam J, Putasaeng B, Yamwong T, Maensiri S: The origin of giant dielectric relaxation and electrical responses of grains and grain boundaries of W-doped CaCu₃Ti₄O₁₂ ceramics. J Appl Phys 2012, 112:114115.
- Liu L, Fan H, Fang P, Chen X: Sol–gel derived CaCu₃Ti₄O₁₂ ceramics: synthesis, characterization and electrical properties. *Mater Res Bull* 1800, 2008:43.
- Kashyap R, Thakur OP, Tandon RP: Study of structural, dielectric and electrical conduction behaviour of Gd substituted CaCu₃Ti₄O₁₂ ceramics. *Ceram Int* 2012, 38:3029.
- Sulaiman MA, Hutagalung SD, Ain MF, Ahmad ZA: Dielectric properties of Nb-doped CaCu₃Ti₄O₁₂ electroceramics measured at high frequencies. *J Alloys Compd* 2010, 493:486.
- Masingboon C, Eknapakul T, Suwanwong S, Buaphet P, Nakajima H, Mo SK, Thongbai P, King PDC, Maensiri S, Meevasana W: Anomalous change in dielectric constant of CaCu₃Ti₄O₁₂ under violet-to-ultraviolet irradiation. *Appl Phys Lett* 2013, 102:202903.
- Bastús NG, Comenge J, Puntes V: Kinetically controlled seeded growth synthesis of citrate-stabilized gold nanoparticles of up to 200 nm: size focusing versus ostwald ripening. *Langmuir* 2011, 27:11098.
- 22. Nan CW, Shen Y, Ma J: Physical properties of composites near percolation. *Annu Rev Mater Res* 2010, **40**:131.
- Dang Z-M, Yuan J-K, Zha J-W, Zhou T, Li S-T, Hu G-H: Fundamentals, processes and applications of high-permittivity polymer-matrix composites. *Prog Mater Sci* 2012, 57:660.
- 24. Nan C-W: Physics of inhomogeneous inorganic materials. *Prog Mater Sci* 1993, **37:**1.
- 25. Adams TB, Sinclair DC, West AR: Giant barrier layer capacitance effects in CaCu₃Ti₄O₁₂ ceramics. *Adv Mater (Weinheim, Ger)* 2002, 14:1321.
- Pecharromán C, Iglesias J: Effective dielectric properties of packed mixtures of insulator particles. *Phys Rev B Condens Matter* 1994, 49:7137.
- Ribeiro WC, Araújo RGC, Bueno PR: The dielectric suppress and the control of semiconductor non-Ohmic feature of CaCu₃Ti₄O₁₂ by means of tin doping. *Appl Phys Lett* 2011, 98:132906.

- Ramírez MA, Bueno PR, Varela JA, Longo E: Non-Ohmic and dielectric properties of a CaCu₃Ti₄O₁₂ polycrystalline system. *Appl Phys Lett* 2006, 89:212102.
- Thongbai P, Putasaeng B, Yamwong T, Maensiri S: Improved dielectric and non-ohmic properties of Ca₂Cu₂Ti₄O₁₂ ceramics prepared by a polymer pyrolysis method. J Alloys Compd 2011, 509:7416.

doi:10.1186/1556-276X-8-494

Cite this article as: Tuichai *et al.*: **Dramatically enhanced non-Ohmic** properties and maximum stored energy density in ceramic-metal nanocomposites: CaCu₃Ti₄O₁₂/Au nanoparticles. *Nanoscale Research Letters* 2013 8:494.

Submit your manuscript to a SpringerOpen[™] journal and benefit from:

- ► Convenient online submission
- ► Rigorous peer review
- Immediate publication on acceptance
- Open access: articles freely available online
- ► High visibility within the field
- Retaining the copyright to your article

Submit your next manuscript at > springeropen.com