Dramatically enhanced non-Ohmic properties and maximum stored energy density in ceramic-metal nanocomposites: CaCu$_3$Ti$_4$O$_{12}$/Au nanoparticles

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Abstract

Non-Ohmic and dielectric properties of a novel CaCu$_3$Ti$_4$O$_{12}$/Au nanocomposite were investigated. Introduction of 2.5 vol.% Au nanoparticles in CaCu$_3$Ti$_4$O$_{12}$ ceramics significantly reduced the loss tangent while its dielectric permittivity remained unchanged. The non-Ohmic properties of CaCu$_3$Ti$_4$O$_{12}$/Au (2.5 vol.%) were dramatically improved. A nonlinear coefficient of $\approx 17.7$ and breakdown electric field strength of $1.25 \times 10^4$ V/m were observed. The maximum stored energy density was found to be 25.8 kJ/m$^3$, which is higher than that of pure CaCu$_3$Ti$_4$O$_{12}$ 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 ($\varepsilon'$) have been intensively studied because of their potential for multilayer ceramic capacitor applications. The dielectric materials used in these devices must exhibit a high $\varepsilon'$ with very low loss tangent (tan$\delta$). 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 $U = \varepsilon' \varepsilon_0 E_b^2/2$, where $E_b$ 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 $\varepsilon'$ [2-11]. Generally, $\varepsilon'$ increases rapidly in the region of the percolation threshold (PT) [4,9]. For the Ag-Ba$_{0.75}$Sr$_{0.25}$TiO$_3$ composite [9], the large increase in $\varepsilon'$ was suggested to result from the percolation effect. Improved tunability of Ba$_{0.75}$Sr$_{0.25}$TiO$_3$ ceramics 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].

CaCu$_3$Ti$_4$O$_{12}$ (CCTO) is one of the most interesting ceramics because it has high $\varepsilon'$ 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$\delta$ (>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 ($\alpha$) and $E_b$ values. For energy storage devices, both $\varepsilon'$ and $E_b$ 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$_3$Ti$_4$O$_{12}$ powder was prepared by a solid state reaction method. First, CaCO$_3$, CuO, and TiO$_2$ were mixed homogeneously in ethanol for 24 h...
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 nanocomposites 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 G², 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 10² to 10⁷ 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) – 2188 and the minor phase of Au filler could be well described by Eq. (1). From the fitted result, the percolation effect [4,7,9,17,22-24]. A rapid increase in the depolarization effect [4,7,9,17,22-24] of the composites can be described by the power law [4,9,22,24]:

\[
\varepsilon'_{\text{eff}} = \varepsilon'_{\text{matrix}} \left( \frac{f_c - f_c^q}{f_c^q} \right)^q,
\]

where \( \varepsilon'_{\text{matrix}} \) is the dielectric constant of the insulator matrix, \( f_c \) is the PT, \( f_c^q \) is the volume fraction of conductive filler, and \( q \) is a critical component. As shown in Figure 3, the dependence of \( \varepsilon' \) on the volume fraction of Au NPs can be well described by Eq. (1). From the fitted result, \( f_c^q \) 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]. \( f_c^q \) 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 \((q \approx 0.8 \text{ to } 1)\), indicating a slow increase in \(\varepsilon'\) 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 Ba0.75Sr0.25TiO3/Ag \((f_c = 0.285)\) [9] and BaTiO3/Ni \((f_c = 0.232 \text{ to } 0.310)\) [4,7] microcomposite systems. In the cases of the nanocomposite systems of PbTiO3/Ag [8] and Pb0.4Sr0.6TiO3/Ag [11], \(f_c\) values were found to be 0.16. Actually, the obtained \(f_c\) 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 Ba0.75Sr0.25TiO3/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 obtain \(f_c \approx 0.16\). 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 \(f_c < 0.16\). 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 $\varepsilon'$ 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 $\mu$m) in the microstructure of CCTO/Au3 and CCTO/Au4 (data not presented), the large observed enhancement of $\varepsilon'$ 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 $E_b$. Figure 4 shows the non-Ohmic properties of the CCTO/Au nanocomposites as a plot of electrical current density ($J$) vs. electric field strength ($E$). $\alpha$ values of the CCTO, CCTO/Au1, CCTO/Au2, CCTO/Au3, and CCTO/Au4 samples were calculated in the range of $J = 1$ to 10 mA/cm² and found to be 7.38, 17.67, 11.08, 5.05, and 3.08, respectively. $E_b$ values (obtained at $J = 1$ mA/cm²) were found to be $4.26 \times 10^3$, $1.25 \times 10^4$, $1.17 \times 10^5$, $2.50 \times 10^5$, and $7.84 \times 10^5$ V/cm, respectively. $\alpha$ and $E_b$ 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 $E_b$. This observation is consistent with the effective medium theory [26]. Therefore, it is reasonable to suggest that the increases in $\varepsilon'$ and tan$\delta$ 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 CaCu$_3$Ti$_{3.8}$Sn$_{0.2}$O$_{12}$ 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 tanδ, while ε’ was unaltered. The non-Ohmic properties of this composition were also successfully improved showing α = 17.7 and E_b = 1.25 x 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 increased. 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 program of Center of Excellence Network. This work was financially supported by the Nanotechnology Center (NANOTEC), NSTDA, Ministry of Science and Technology, Thailand, through Nanotechnology Center for the study. All authors read and approved the final manuscript.

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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.