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Ceramics International 38S (2012) S249–S253

CERAMICS INTERNATIONAL

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Microstructure and electrical properties of $BaTiO_3$/Cu ceramic composite sintered in nitrogen atmosphere

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Abstract

$BaTiO_3/x$Cu composite ceramics with $x = 0–30$ wt.% were fabricated by the traditional mixing oxide method and their microstructure, relative density, electric conductivity, permittivity and dielectric loss were measured as a function of the Cu mass fraction. The X-ray diffraction (XRD) patterns indicated that the dense composite has no chemical reaction between $BaTiO_3$ and Cu during sintering, and the relative diffraction intensity of Cu increased with the increase of Cu. The electric properties showed that the percolation threshold of $BaTiO_3$/Cu composites was $x = 0.25$ and its conductivity increased as the Cu content increased after that. With increasing Cu content up to 30 wt.%, the permittivity (ε_r) markedly increased from ~3000 for monolithic $BaTiO_3$ to ~8000 at 1 kHz. Additionally, the temperature coefficient of this system was less than 5% in the temperature range of 25–115°C.

Keywords: B. Composite; C. Dielectric properties; Microstructure; Percolation theory

1. Introduction

The influences of metallic phases in ferroelectric and paraelectric materials have been investigated for various combinations such as PZT/Ag [1], PZT/Pt [2], $BaTiO_3$/Ni [3], $BaTiO_3$/Cr [4] and $SrTiO_3$/Pt systems [5], which typically show very high dielectric constants and have been of special interest for applications related to energy storage. Often, these metallic doped composites have unique features that are distinct from the regular monolithic material. In general, these features occur in materials filled with inclusions such as highly conducting fibre distributed randomly in a host, which could demonstrate an insulator–metal transition with increasing metal concentration [9]. The results show that the metallic phase acts as a bridge within the ceramic and not only improves the mechanical properties, but, according to the percolative phenomenon [6], also changes the electrical properties of the matrix, such as the piezoelectrical properties, permittivity (ε_r) and electrical conductivity. However, it has been very difficult to experimentally observe the phenomena occurring at the percolation threshold, and only a few groups have reported the effect of a strongly enhanced permittivity for ceramic–metal composites in the neighborhood of the percolation threshold [7,8]. A dielectric characteristics study of the ceramic–metal composites indicated that the composite's response to an applied electric field may be attributed to different types of polarization, which may be affected by varying the temperature or the electric field frequency [2].

Some high ε_r ferroelectric $BaTiO_3$ ceramics could be obtained by doping with Pt, Ag and other noble metals. It is interesting to study the sintering properties and dielectric characteristics of this material that are brought about by adding Cu as the metallic phase in the $BaTiO_3$ matrix. In our paper, the effects of doping Cu metal into $BaTiO_3$ on its microstructure and dielectric properties were investigated with the purpose of developing a novel temperature-stable, high ε_r $BaTiO_3$ dielectrics.

2. Experimental

The starting materials were commercially available $BaTiO_3$ (>99.9%) and Cu powders (>99.8%). First, $BaTiO_3$ and Cu powders were mixed with copper content of 0, 5, 10, 15, 20, 25, 30 wt.% by ball milling for 4 h. Then, the slurry was dried and sieved with 150 μm mesh. Next, green compacts were formed

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doi:10.1016/j.ceramint.2011.04.094

by stainless steel mold. The samples were sintered at 1290 °C in N_2 flow for 2 h.

Density measurements of the sintered samples were carried out on the basis of the Archimedes principle. X-ray diffraction (D/max2200pc, 2002, Rigaku, Tokyo, Japan) was used to identify the phase regarding the sintered composite discs, and the microstructural characterization of composite discs was carried out using a scanning electron microscope (JEOL JSM-6390A JEOL Ltd., Tokyo, Japan). To visualize the element distributions of Ba, Ti, and Cu, analytical SEM by energy–depressive X-ray spectroscopy (EDS) was performed. Finally, the polished samples were coated with In–Ga as the electrodes for measuring of electric properties. The dielectric loss and frequency dependence of permittivity were evaluated in frequency range 10^2–10^6 Hz using the Agilent impedance analyzer (E4980A, Agilent Tech., CA, USA). The temperature dependence of permittivity (HP4284A, Agilent Tech., CA, USA) was carried out from room temperature to 160 °C.

3. Results and discussion

The XRD patterns of the sintered $BaTiO_3$/Cu composites are shown in Fig. 1. All peaks were attributed to either the $BaTiO_3$ phase or Cu without any impurities being observed, which suggests that no reaction took place between $BaTiO_3$ and Cu during the sintering. The relative diffraction intensity of Cu increased with the increase of Cu, which was expected. Fig. 2 shows the apparent and relative density of $BaTiO_3$/Cu composites. The apparent density of $BaTiO_3$/Cu composites increased with increasing amount of Cu.

The SEM images of the composites with different content of Cu and the EDS spectra of $x = 30$ wt.% are shown in Fig. 3. It was seen in Fig. 3(a) and (b) that abnormal grain growth was clearly observed. The normal grain size of pure $BaTiO_3$ was about 1 μm, while the abnormal grain size of $BaTiO_3$/Cu composites was about 50 μm. Abnormal grain growth was generally known to occur when particle shape was angular in the presence of liquid phase during sintering [10]. It is indicated that the low eutectic liquid phase formed between Cu and $BaTiO_3$ during sintering promoted the grain growth [15]. In Fig. 3(c), lots of big spheroidal copper particles stood in the $BaTiO_3$ matrix. That is the Cu agglomerated with increasing amount of Cu. The coalescence of Cu may be caused by pores, which also contributes to the decrease of relative density of $BaTiO_3$/Cu composites with increasing amount of Cu. And the spheroidal copper particles on the surface of $BaTiO_3$ matrix (Fig. 3(d)) were identified as Cu by EDS analysis (Fig. 3(e)).

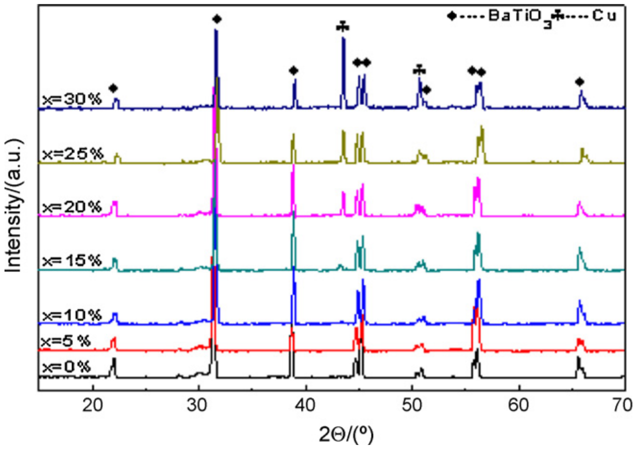

Fig. 1. X-ray diffraction patterns of $BaTiO_3$/Cu composites sintered at 1290 °C in N_2 flow for 2 h.

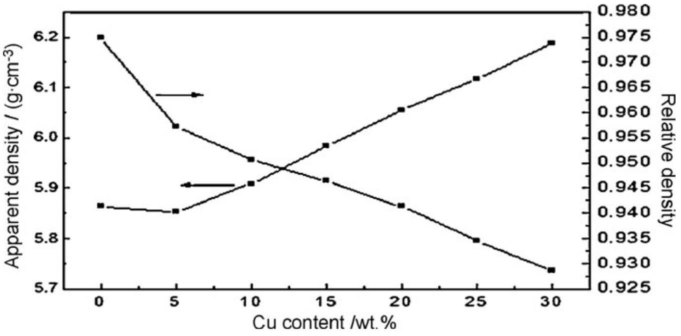

Fig. 2. Apparent and relative density of $BaTiO_3$/Cu composites sintered at 1290 °C in N_2 flow for 2 h.

The conductivity of $BaTiO_3$/Cu composites is shown in Fig. 4. When the Cu content was 5 wt.%, the conductivity was $\sim 7.4 \times 10^{-4}$ S m^{-1}, and the percolation threshold, which is denoted by a nonlinear transition, occurred when the Cu concentration was 25 wt.%. Above the percolation threshold, the conductivity of the composites raise further but at a slower rate, which could be explained by the percolative phenomenon and the diagram of the conductivity model in Fig. 5. According to the percolation theory [11]

$$\sigma \propto \sigma_M (f - f_c)^t \quad f > f_c \tag{1}$$

$$\sigma \propto \sigma_D (f_c - f)^{-q} \quad f < f_c \tag{2}$$

where σ, σ_M, σ_D are the conductivity of composite materials, conductors and insulators (dielectric), respectively, f_c is the percolation threshold, and t and q are the critical exponents though there has not yet been a unified understanding about the critical indices' values in academia. Still, the conductivity of the $BaTiO_3$/Cu composites followed Eq. (1) when the copper content was lower than percolation threshold ($f < f_c$), and the conductivity was close to that of the conductor due to the conductive particles dispersed into the matrix in clusters as shown in the model on the left in Fig. 4. Additionally, when the amount of Cu was higher than percolation threshold ($f > f_c$), as described by Eq. (2), the conductive particles gathered into larger clusters and were interconnected into an infinite cluster; when Cu reached the critical amount, it formed a conductive pathway as shown in the model on the right in Fig. 4.

Fig. 5 shows the permittivity and dielectric loss of $BaTiO_3$/Cu composites with different Cu content as a function of the frequency (a and b) of the applied electric field and temperature (c). As shown in Fig. 5(a), the permittivity increased with increasing Cu content and attained a value of ~3000 when the Cu concentration was 5 wt.% and ~8000 when concentration was 30 wt.%. Furthermore, the variation in permittivity from a frequency of 100 Hz to 2 MHz decreased distinctly.

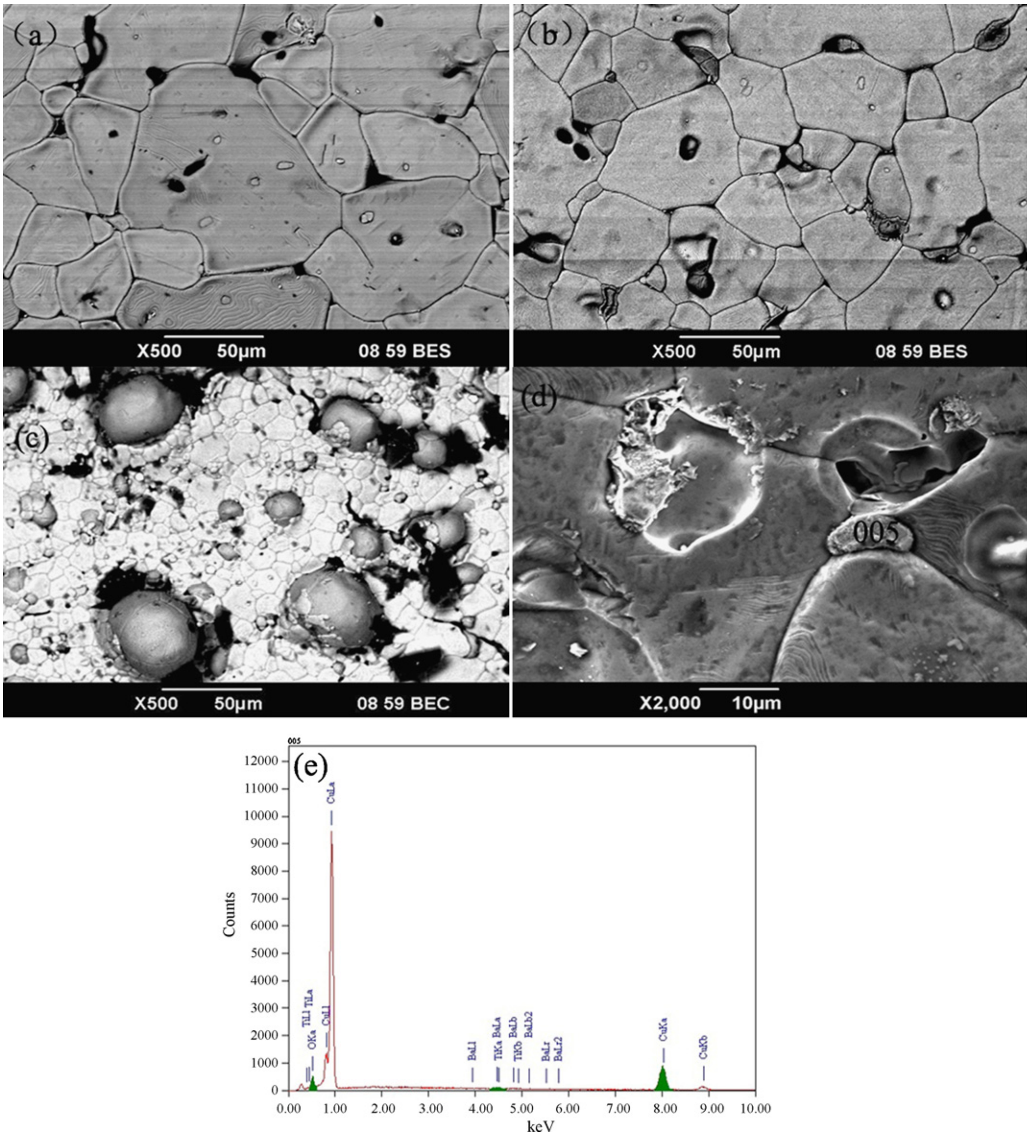

Fig. 3. SEM images of the surface of $BaTiO_3$/*x*Cu composites sintered at1290 °C for 2 h in N_2 flow: (a) $x = 5$ wt.%; (b)$x = 20$ wt.%; (c) $x = 30$ wt.% and SEM image and EDS spectra of $x = 30$ wt.% (d and e).

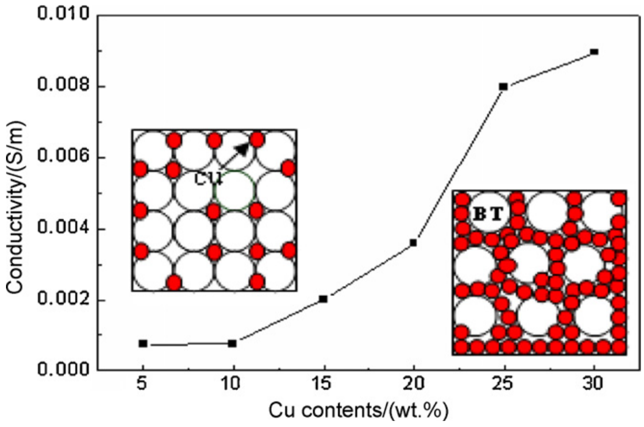

Fig. 4. Conductivity of $BaTiO_3$/Cu composites sintered at 1290 °C in N_2 flow.

This variation of the permittivity is due to changes in the four basic mechanisms which affect the polarization, α_t; the mechanisms, in the order of their response times, are the electronic polarization [α_e], ionic polarization [α_i], dipolar polarization [α_o] and the space charge [α_s]. These yield the following system $\alpha_t = \alpha_e + \alpha_i + \alpha_o + \alpha_s$ [12,13]. The electronic polarization [α_e] is active at atomic vibrations and optical frequencies and beyond, ionic polarization [α_i] is affected at infrared frequencies ($\approx 10^{13}$ Hz). The space charge [α_s] mechanism could require some time to build up and, therefore, corresponds to fractions of a kHz. The space charge mechanism had an important role in this system, because there were many space charges generated between $BaTiO_3$ and Cu, and the quantity of space charges rose with the increasing amount of Cu. Consequently, the permittivity of $BaTiO_3$/Cu composites increased significantly with increasing Cu content, and the

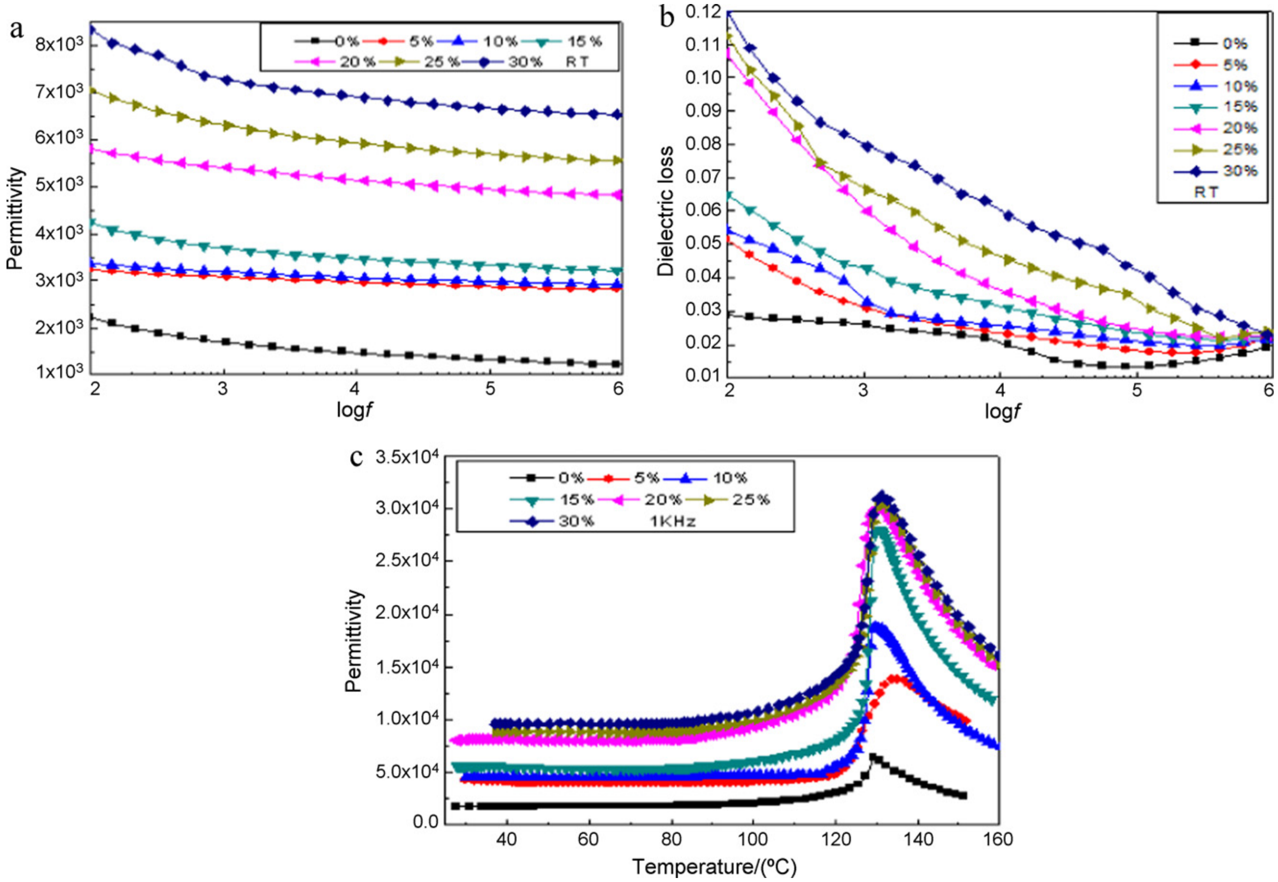

Fig. 5. Dependence of permittivity (a) and dielectric loss (b) of $BaTiO_3$/Cu composites on frequency at room temperature and temperature (c) at 1 kHz sintered at 1290 °C in N_2 flow.

maximum value was ~8000 when the concentration was 30 wt.% at 1 kHz. This large increase in permittivity at the lower frequencies was mainly attributed to polarization due to the space charge mechanism as well. When the applied frequency was much higher than the natural frequency of the dipole, the dipole was not able to react and consequently did not contribute to the permittivity.

The frequency dependence of dielectric loss of $BaTiO_3$/Cu composites is shown in Fig. 5(b). The dielectric loss increased with increasing Cu content and decreased with increasing frequency from 100 Hz to 1 MHz due to the raised of conductance loss and reduced of the space charge polarization. Dependence of permittivity and dielectric loss of $BaTiO_3$/Cu composites on frequency could also be explained by percolation theory [11]

$$\varepsilon = \varepsilon_D \left| \frac{f_c - f}{f_c} \right|^{-q} \tag{3}$$

where ε, ε_D are the permittivity of composites and the matrix, respectively. When $f < f_c$, as the permittivity increases, the dielectric loss was not increased significantly with increasing Cu content. This was because the introduction of metal phase generally causes the increasing of dielectric loss, but the dielectric properties of $BaTiO_3$ was closely related to the internal stress and grain size of the $BaTiO_3$ [14], the introduced flexible metal particles could reduce the internal stress of the dielectric loss at a great degree, which can be seen from $x = 0$–20 wt.% in Fig. 5(b). But as Cu content reached to f_c, the conductivity increased and the conductance loss increased obviously resulting in dielectric loss began to increase significantly.

The variation in the permittivity from room temperature to the peak temperature (130 °C) was 3.12×10^4 when the Cu concentration was 30 wt.%, as shown in Fig. 5(c). Below the transition temperature, the permittivity increased very little as the temperature increased to 115 °C, which indicated that $BaTiO_3$/Cu composite ceramics were stable within that temperature range and useful as large ε_r $BaTiO_3$ dielectrics.

4. Conclusions

$BaTiO_3$/Cu composite ceramics without other secondary phases were prepared using a traditional solid-phase method. Resistivity of the $BaTiO_3$/Cu composite ceramics increased with increasing Cu content and followed the percolation theory with the percolation threshold of the $BaTiO_3$/Cu composite being 25 wt.%. The permittivity increased as the amount of Cu increased and attained the value of ~3000 when the concentration was 5 wt.% and ~8000 when it was 30 wt.% at 1 kHz. Below the transition temperature (130 °C), the temperature coefficient of composite ceramics was less than 5%

in the temperature range 25–115 °C, and thus the ceramic would be a highly stable dielectric with high permittivity.

Acknowledgments

This research has been supported by the Key Project of Chinese Ministry of Education (209126, Research Projects of Science and Technology Division, Shaanxi (2010K10–14), Foundation of Shaanxi Educational Committee (112H011). We thank for the support by the Graduate Innovation Fund of Shaanxi University of Science and Technology.

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