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Enhancement of dielectric properties by additions of Ni nano-particles to a X7R-type barium titanate ceramic matrix

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Abstract

Some different amounts of nano-sized Ni powder (from 1 to 30 vol.%) have been mixed with $BaTiO_3$-based EIA X7R ceramic powders used in base metal electrode (BME) multilayer ceramic capacitors (MLCC). The X-ray diffraction (XRD) analysis indicated that no phases other than $BaTiO_3$ and Ni were present in the doped ceramics and further suggested that no reaction took place between $BaTiO_3$ and Ni during sintering under reducing atmosphere. The scanning electronic microscope (SEM) observation showed that the Ni particles presented homogeneous distribution in $BaTiO_3$ ceramic matrix. It was found that the relative density decreased with increasing Ni-content while the dielectric constant at broad temperature range increased. The dielectric constant at room temperature of the ceramic with Ni-content of 28 vol.% is about 6000, 2.5 times of Ni-free ceramics, 2500. When Ni-content is 30%, the ceramic became a conductor. The temperature coefficient of capacitors (TCC) of the ceramics showed decline with the increase of Ni-content. The percolation theory of insulator–metal transitions can explain the enhancement of dielectric constant. The percolation threshold of the ceramic–metal composites for dielectric constants at room temperature, f_c, is 37 vol.% and the critical exponent, p, is 0.6. The dielectric losses, tgδ showed the similar phenomena with ε.

Keywords: B. Composites; C. Dielectric properties; D. $BaTiO_3$; E. Capacitors

1. Introduction

Barium titanate ($BaTiO_3$, BT), a perovskite structure, has been widely investigated because of its dielectric and ferroelectric properties [1,2]. It is obvious that replacing the precious metal with base metal in multilayer ceramic capacitors (MLCC) can significantly reduce the production costs. The best candidate for such a replacement was Ni. To protect Ni from being oxidized during the co-firing process, it is necessary to fire base metal electrode (BME)-MLCC in reducing atmospheres.

It has been observed that for X7R capacitors (i.e. temperature coefficient of capacitance could be within the range of ±15% between −55 and 125 °C), dielectric constant of capacitors in the multilayer form is about 15–20% higher than that in the disc form. So it is assumed that the dielectric properties can be improved significantly by adding metallic inclusions [3,4]. Hwang et al.[5] reported that due to the plasticity of metal particles, the internal stresses of multilayer structures induced during the sintering process can be relaxed. Chen and Tuan [6] studied the effect of Silver on the sintering and grain-growth behaviors of $BaTiO_3$, and the mechanical and dielectric properties of $BaTiO_3$–Ag composite [7] with the grain size bigger than 10 μm. Carlos Pecharromán et al. [8] reported ultra-high dielectric constant, 80 000 of the composites matured by pure $BaTiO_3$ and Ni. But the Ni particle size in ceramic matrix is about 3 μm, which cannot be used for MLCC with ultra-thin layers less than 10 μm.

In this paper, we studied the dielectric properties of the composites containing X7R-type $BaTiO_3$ ceramics for BME-MLCC and Ni nano-particles to find out a composition adaptable with thin layer procedures.

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2. Experimental

Fine barium titanate powders (100 nm, Shandong Guoteng Co.) were calcined at 1000 °C for 2 h. Then these powders were mixed with MgO and some rare earth oxides to obtain X7R ceramics for BME-MLCC. The nickel particle size is 50 nm. X7R powders and various amounts (0–30 vol.%) of Ni were ball-milled together in ethanol. Pellets were made from the mixed powder under a pressure of 5 MPa. The sintering process was divided into three steps: (i) at 400 °C for 0.5 h in a 90%N_2/10%H_2 atmosphere in order to reduce the NiO on of the starting Ni particles; (ii) at 1300 °C under a 90%N_2/10%H_2 atmosphere for 2 h for final sintering; (iii) annealed in a weak oxidizing atmosphere at 1000 °C.

Phase identification was performed by X-ray diffractometry (XRD Rigaku D/Max B) on the ceramic discs. The surfaces of these samples were observed by SEM (JEOL JSM6301F) with EDX analysis. The experimental density was determined using Archimedes' method. Silver paste was coated on both surfaces of samples as electrodes. The temperature dependence of the dielectric constant was measured at temperatures ranging from −60 to 150 °C using a LCR meter (HP 4192) at 1 kHz and 1 V_{rms}.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the ceramics. The XRD analysis indicated that no phases other than $BaTiO_3$ and Ni were present in the ceramics, and further suggested that no reaction took place between $BaTiO_3$ and Ni during sintering. The relative diffraction intensity of Ni metal increased with the Ni-content.

Fig. 2 shows the surface microstructures of the samples with 4, 18, 26 vol.% Ni and EDX analysis of the sample with 18 vol.% Ni. Fig. 2a–c are SEM images. The grain sizes of ceramic matrix show relatively uniform distribution and the average grain size of the ceramics is about 0.4 μm. The EDX analysis of sphere-like clusters suggested that Ni existed in the form of metal. These clusters were composed by the nano-particles. The Ni cluster size increases with the Ni-content. Ni nano-particles show in cluster state. These clusters distributed disorderly in ceramic matrix and were isolated from each other by the $BaTiO_3$ matrix.

Fig. 3 shows the curve of the density of samples versus Ni-content. The experimental density increases with Ni-content almost linearly, while the relative density decreases. The theoretical density of these samples is computed from the theoretical densities of $BaTiO_3$ (6.01 g/cm^3) and Ni (8.908 g/cm^3) according to the normal Ni-content. The decrease of the relative density means that the porosity increases with the increasing of Ni-content.

Ni metal nano-particles have a significant effect on the dielectric behavior of the Ni–$BaTiO_3$ composites. The variations in the dielectric constants with temperature for the composites are shown in Fig. 4. The dielectric constants at temperatures from −60 to 150 °C increased with Ni-content. The temperature coefficient of capacitors (TCC) calculated from dielectric constants declined with the increase of Ni-content. When Ni-content is 28 vol.%, the maximum TCC of the disc sample is close to −15%. The TCC will rotate clockwise around 25 °C to meet X7R specifications. So the composites can be used for BME-MLCC. The improvement in dielectric constant was not significant compared with that reported by Carlos Pecharromán et al. [8]. It may be affected by the increased porosities.

This enhancement of dielectric properties can be explained by percolation theory. As shown in Fig. 5a, the percolation transition is obviously observed, the dielectric constant at room temperature of the composite with Ni-content of 28 vol.% reaches as high as 6000, which is about 2.5 times larger than that of the Ni-free ceramics. When Ni-content was 30 vol.%, the composites became a conductor. The enhancement in the dielectric constant at room temperature can be explained according to the following power law [9]:

$$\langle \varepsilon \rangle = \varepsilon_0 \left| \frac{f_c - f}{f_c} \right|^{-q} \tag{1}$$

where $\langle \varepsilon \rangle$ is the dielectric constants of the Ni–$BaTiO_3$ composites, ε_0 is the dielectric constant of Ni-free sample, f is the filling factor of Ni-content, f_c is the percolation threshold, and q is a critical exponent. The experimental values of effective relative dielectric constant are in good agreement with Eq. (1), with $f_c = 0.37$ and $q = 0.6$. It should be noted that the value of the percolation threshold is abnormally high, which is consistent with reported by Carlos Pecharromán et al. [8]. According to the percolation theory of random composites, the percolation threshold of the two-phase random composite is about $f_c = 0.16$. The differences of percolation threshold were studied by Stau.er

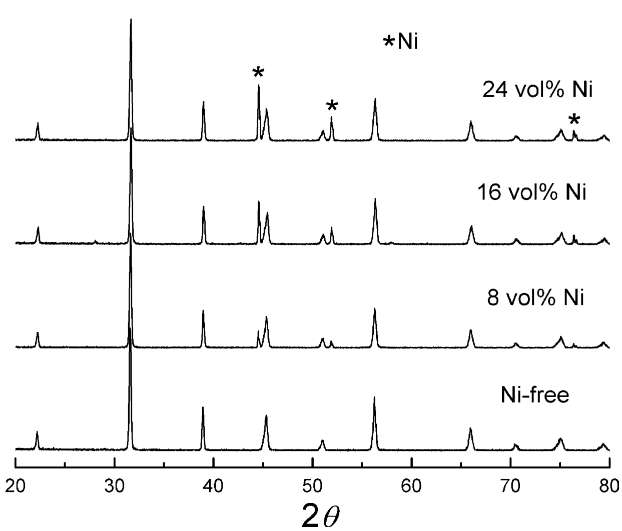

Fig. 1. XRD patterns of X7R ceramics doped with different contents of nickel.

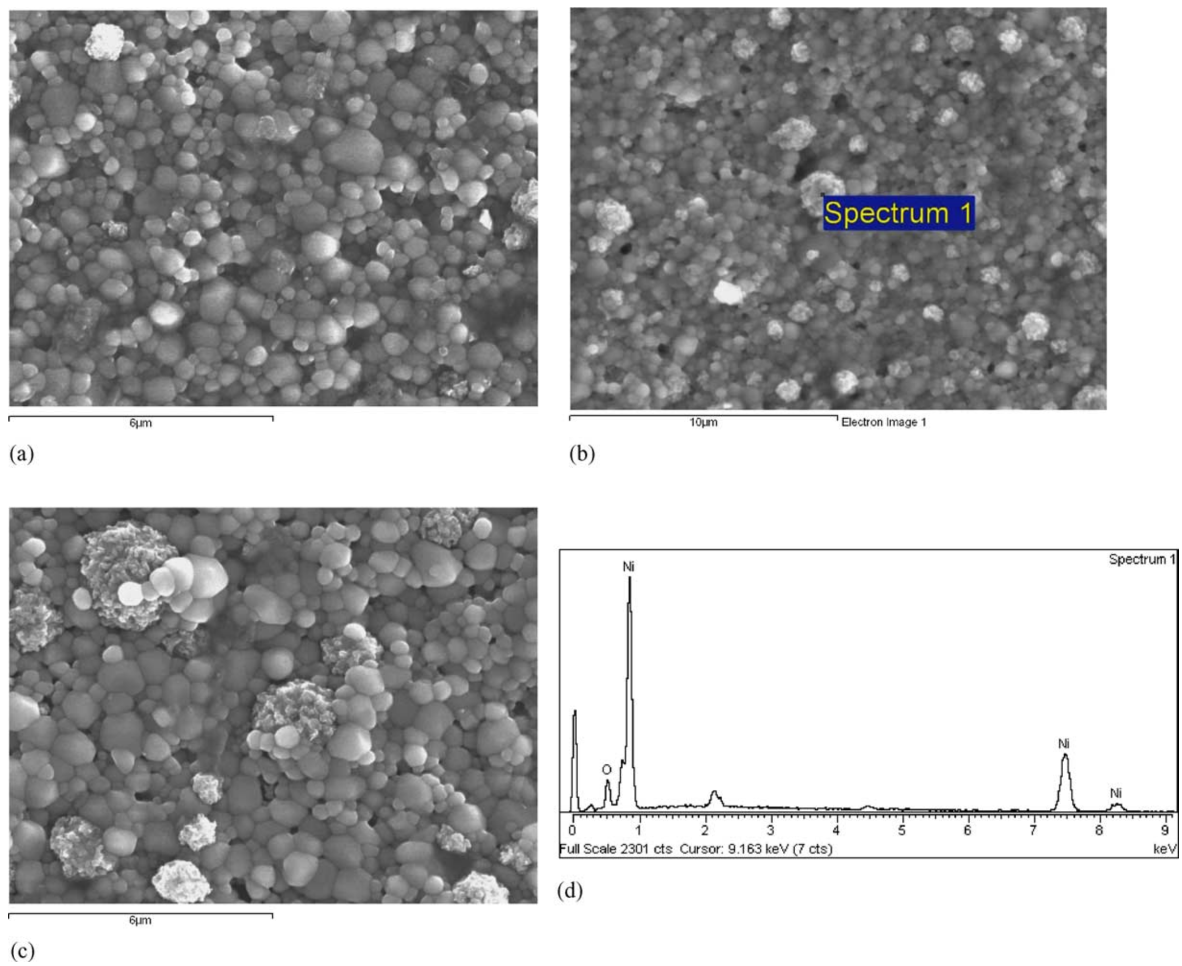

Fig. 2. Surface SEM images and EDX analysis of ceramic samples: (a) 4 vol.% Ni, 10 000×; (b) 18 vol.% Ni, 5000×; (c) 26 vol.% Ni, 10 000×; (d) EDX analysis of the sphere cluster labeled as Spectrum 1 in (b).

and Zabolitzky [10]. As they reported, $f_c = 0.33$ suggested that the two phases in the composites had similar geometrical shapes while $q = 0.735$ meant that the composites had homogeneous microstructure and no preferred asymmetry [10]. Since the microstructures shown in Fig. 2 were consistent with the above precondition, the results of percolation calculations can be explained.

The dielectric losses of Ni–$BaTiO_3$ composites showed similar phenomena as seen in Fig. 5b. The variation of tgδ

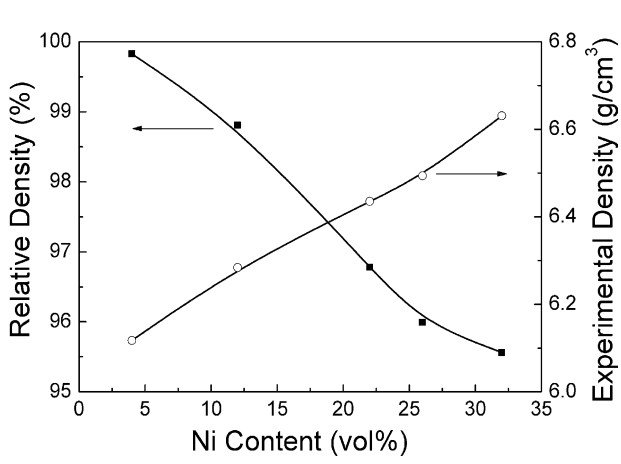

Fig. 3. Plot of experimental and relative densities of sintered ceramics vs. Ni-content.

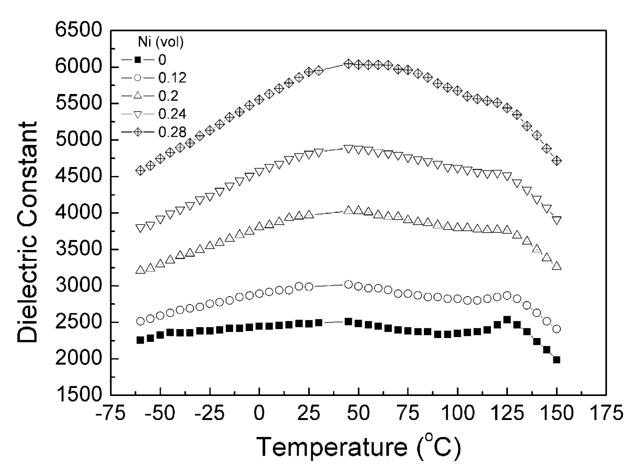

Fig. 4. The dielectric constants of the Ni–X7R composites as a function of temperature at 1 kHz.

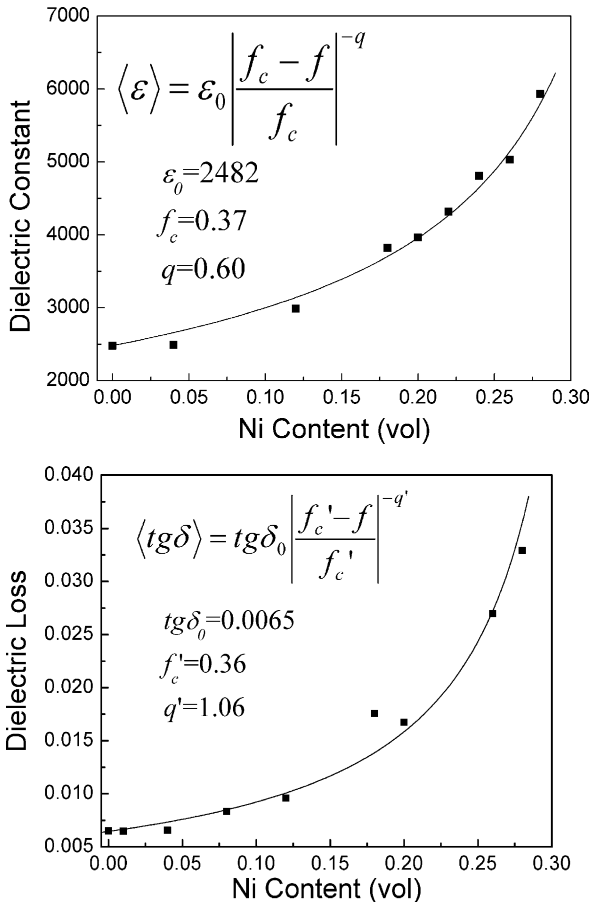

Fig. 5. Variation of the dielectric constant (a) and dielectric loss (b) vs. Ni volume fraction at 1 kHz and 25 °C.

at room temperature with Ni-content can be formulated in Eq. (2).

$$\langle \mathrm{tg}\delta\rangle = \mathrm{tg}\delta_0 \left|\frac{f_c' - f'}{f_c'}\right|^{-q'} \tag{2}$$

where $\langle \mathrm{tg}\delta\rangle$ is the dielectric losses of the Ni–$BaTiO_3$ composites, $\mathrm{tg}\delta_0$ is the dielectric loss of Ni-free sample, f' is the filling factor of Ni-content, f_c' is the percolation threshold, and q' is a critical exponent for $\mathrm{tg}\delta$. f_c' was 0.36, accord with that of dielectric constant and q' was 1.37, which means the increase rate of $\mathrm{tg}\delta$ was bigger than that of ε.

As can be deduced from Fig. 5a and b, $f = 0.6 f_c$–$0.9 f_c$ seems to be the optimal composition range in which to design a percolative MLCC, because for these compositions relatively large values of dielectric constant with low losses.

4. Conclusions

The dielectric properties of the Ni–X7R composites were investigated. Ni did not react with $BaTiO_3$ during sintering, and Ni particles showed homogeneous distribution in ceramics. Metal Ni nano-particles can increase the dielectric constant of the composites. The percolation threshold is 0.37. These composites can be used for BME-MLCC with ultra-thin layers.

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