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International Journal of Minerals, Metallurgy and Materials
Volume 16, Number 3, June 2009, Page 345

Materials

Effect of milling process on the core-shell structures and dielectric properties of fine-grained $BaTiO_3$-based X7R ceramic materials

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(Received 2008-06-01)

Abstract: Fine-grained $BaTiO_3$-based X7R ceramic materials were prepared and the effects of milling process on the core-shell structures and dielectric properties were investigated using scanning electron microscope, transmission electron microscope, and energy dispersive spectroscopy (EDS). As the milling time extends, the dielectric constant of the ceramics increases, whereas the temperature coefficient of capacitance at 125°C drops quickly. The changes in dielectric properties are considered relevant to the microstructure evolution caused by the milling process. Defects on the surface of $BaTiO_3$ particles increase because of the effects of milling process, which will make it easier for additives to diffuse into the interior grains. As the milling time increases, the shell region gets thicker and the core region gets smaller; however, EDS results show that the chemical inhomogeneity between grain core and grain shell becomes weaker.

Key words: fine-grain; barium titanate; core-shell structure; milling process; microstructure; capacitor

[*This work was financially supported by the National Science fund for Distinguished Young Scholars (No.50625204), the National Natural Science Foundation of China (Science Fund for Creative Research Groups)(No.50621201), the Major State Basic Research Development Program of China (No.2009CB623301), the National High-Tech Research and Development Program of China (No.2006AA03Z0428), and Samsung Electro-Mechanics Co., Ltd.*.]

1. Introduction

With rapid development of the electronic industry, multilayer ceramic capacitors (MLCCs) have been widely used in many electronic devices for their properties of high capacitance with small size, high reliability, and excellent high-frequency characteristics. Now, MLCCs trend to have smaller sizes, thinner layer thicknesses, higher capacitances, and base metal as inner-electrode [1-4]. The composition of most dielectric ceramic materials for MLCCs application is based on $BaTiO_3$ (BT), which exhibits high dielectric constant and excellent electrical performance. In order to produce the required temperature-stable characteristics of X7R materials (EIA specifications: dissipation factor of 2.5% or less, temperature coefficient of capacitance (TCC) within the range of ±15% between −55 and 125°C for X7R), pure BT must be modified chemically and physically [5-6]. Donors and acceptors are doped to form chemical inhomogeneity core-shell structures, which have been proved to result in temperature-stable characteristics. In the core-shell structures, the core is ferroelectric pure BT, whereas the shell is paraelectric doped BT [7]. Thus, the flat high-dielectric-constant temperature characteristics can be associated with the high dielectric constant of the core in high-temperature regions and of the shell in low-temperature regions. Hennings reported a formation mechanism of the core-shell structures [8]. The core-shell structures are thermodynamically unstable [9]. Too high sintering temperature will lead to the collapse of the core-shell structures [10]. Moreover, another important factor that will influence the stability of the core-shell structures is donor/acceptor ratio [11-13]. Milling process that is very important in preparing X7R ceramic materials also has a significant influence on the core-shell structures. The degree of damage for BT powder increased during the milling process, the rate of frequency for core-shell grains in micrometer scale ceramics would increase [14]. However, the previous work has focused less on the microstructure evolution of the core-shell structures

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and dielectric properties with different milling time for fine-grained BT-based ceramic materials.

In this work, fine-grained BT-based ceramics with different milling time were prepared, and the effect of milling process on the core-shell structures and dielectric properties of X7R ceramic materials was investigated. The relationship between the dielectric properties and the core-shell structure was discussed as well.

2. Experimental

BT-based ceramics with different milling parameters were prepared by the conventional method. The original pure BT powder was GuoCi's electronic grade BT powder synthesized hydrothermally with the mean grain size of 100 nm. The powder was calcined at 1000°C for 2 h, and the grain size grew up to approximately 350 nm. All the additives (Y_2O_3, MgO, MnO_2, and SiO_2) used here were of reagent grade purity. The calcined BT powder and the additives were mixed by ball milling for different time (A_1 sample: 1 h; A_2 sample: 6 h; A_3 sample: 12 h; A_4 sample: 24 h). The medium used in the milling process was ZrO_2 beads with a diameter of 3 mm. The powder mixtures were subsequently dried and pressed into disks with about 10 mm in diameter and 1 mm in thickness, then sintered at 1250°C for 2 h in a reducing atmosphere followed by a reoxidization process at 1000°C for 3 h. The densities of the sintered ceramics exceeded 5.7 $g\cdot cm^{-3}$.

The surface microstructures of the ceramic samples were observed using a scanning electron microscope (SEM, JSM-6301F, JEOL, Japan). The temperature dependences of the dielectric constant and dielectric loss were measured in the range of −60-150°C at 1 kHz and 1 V (AC) using an impedance analyzer (HP4192A) with a thermostat. Transmission electron microscope (TEM, JEM-2010F, JEOL, Japan) was used to study the core-shell structures of the sintered disc ceramics. Energy dispersive spectroscopy (EDS) microanalysis was performed as well.

3. Results and discussion

SEM micrographs for the surface microstructures of the ceramic samples with different milling time are shown in Fig. 1. All of the samples exhibit fine-grained microstructure with few pores, indicating that the ceramics have been well sintered. It has also been revealed that the grain size of the ceramics, which is approximately 400 nm, does not change much as the milling time extends.

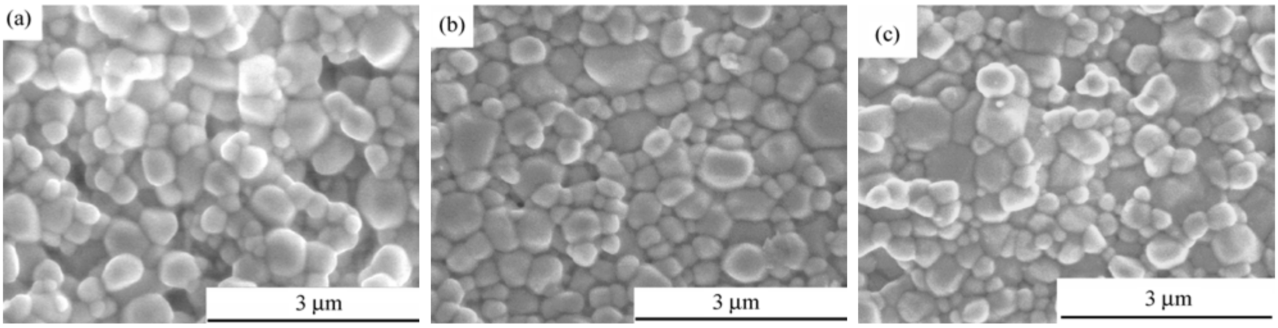

Fig. 1. SEM images of ceramics sintered at 1250°C for 2 h with different milling time: (a) 1 h; (b) 6 h; (c) 24 h.

The dielectric properties of MLCCs are different from those of the bulk ceramics, although the composition of the materials is uniform. When the ceramic materials are fabricated into MLCCs, especially for those with thinner layers, a so-called "clockwise phenomenon" occurs. That means TCC in low-temperature regions increases, whereas it may decrease severely in high-temperature regions. Thereby, in order to achieve a flat dielectric constant-temperature curve for MLCC to satisfy the X7R specification, a higher TCC in the high-temperature regions is essential. The dielectric properties of the samples (A_1 to A_4) milled for different time are shown in Fig. 2. The dielectric constant of the ceramics at 25°C increases from 2500 to 2900 with increasing milling time. On the other hand, TCC at 125°C drops severely from 17% to −12% as shown in Fig. 2(b). When the milling time is longer than 12 h, TCC at 125°C drops to below zero, which may be not very suitable for X7R MLCC application. Moreover, it is obvious that the milling process can change the shape of the dielectric constant-temperature curve. The peak at 125°C is suppressed and the other one at about 40°C is enhanced. The dielectric constants at 25°C and TCC at 125°C for different milling time are summarized in Fig. 3.

TEM micrographs of the ceramics milled for different time (1 h, 6 h, and 24 h) are presented in Fig. 4. All the samples apparently display typical core-shell structures. However, as the micrographs reveal, the volume fraction of the ferroelectric core and the paraelectric shell varies as the milling time changes.

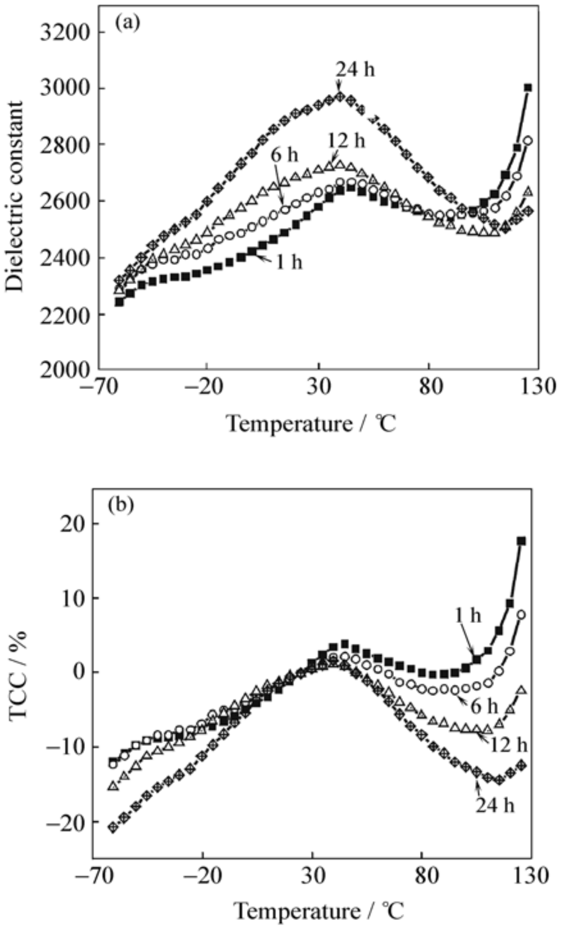

Fig. 2. Dielectric properties of ceramics milled for different time: (a) dielectric constant; (b) TCC.

Fig. 4(a) shows a grain with a very thin shell of about 25 nm, whereas Fig. 4(c) shows a much thicker one. As Fig. 5 reveals, the chemical inhomogeneity between grain core and grain shell gets weaker as the milling time extends. When the milling time is 24 h, it is not easy to distinguish between the grain core and the grain shell from EDS results.

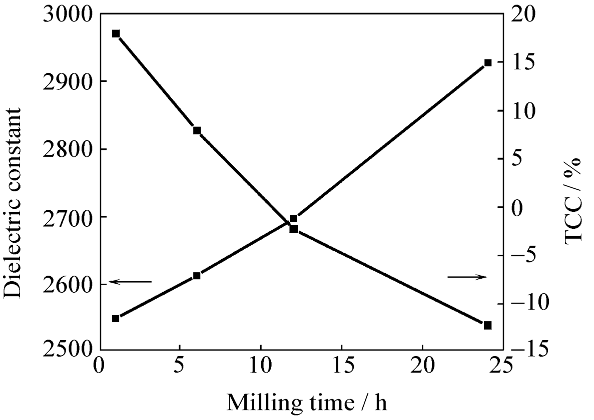

Fig. 3. Dependence of the dielectric constant at 25°C and TCC at 125°C on milling time.

The formation mechanism of the core-shell structure is considered as a process of solid diffusion. During sintering, the dopants diffuse into the interior grain driven by the chemical potential difference resulting from the great concentration gradient. The distance that the dopants can diffuse into the grain will be the thickness of the grain shell. As the milling time extends, the damage that BT particles have been given by the milling process increases, which will increase defects on the surface of BT particles. The specific surface area of specimen A_4 powder, which has been milled for 24 h, increases 6% compared with specimen A_1, which has been only milled for 1 h. The increase of specific surface area is considered to result from the increase of defects on the surface of BT particles. This will make it easier for the dopants to diffuse into the perovskite structures of BT particles.

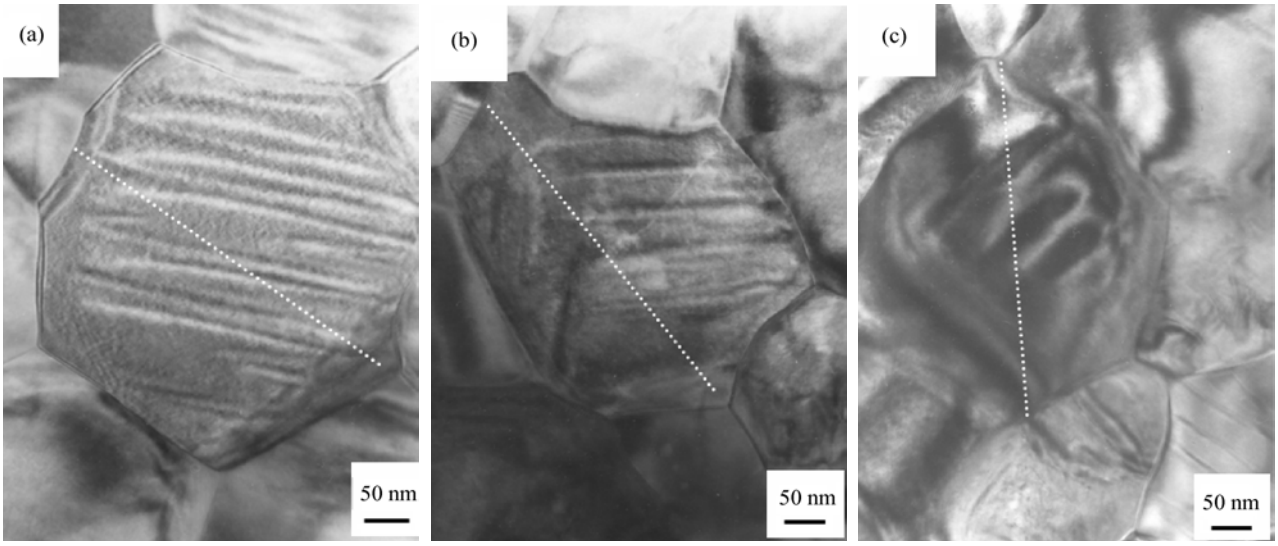

Fig. 4. TEM micrographs of ceramics sintered at 1250°C for 2 h with different milling time: (a): 1 h; (b): 6 h; (c): 24 h.

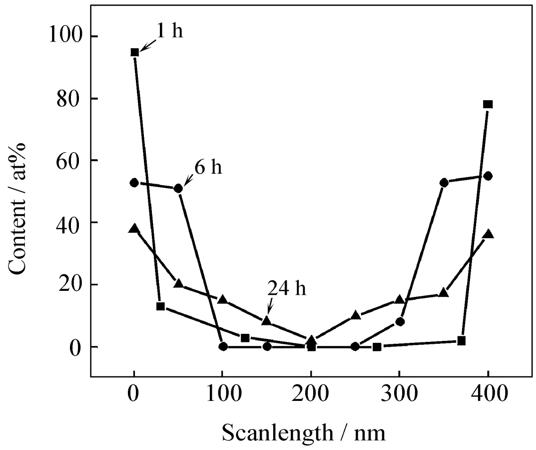

Fig. 5. EDS analysis for yttrium in the core-shell structure of BT based ceramics milled for different time.

As the shell region gets thicker and the core gets smaller, the concentration of the additives in the grain shell also gets lower, and the inhomogeneity between grain shell and grain core becomes weaker. When the milling time is long enough, the additives will spread through the whole grain and the grain will become a uniform solid solution, which leads to the collapse of the core-shell structure. The undoped core exhibits high dielectric constant in high-temperature regions (Curie temperature ~125°C), whereas the doped grain shell exhibits high dielectric constant in low-temperature regions (at about 30-50°C). When the milling time is short and the grain shell is thin, the dielectric properties of the grain are dominated by the core and the ceramics show a relatively low dielectric constant at room temperature and a high TCC at 125°C. In contrast, when the milling time is long and the grain shell is thick, the dielectric property will be dominated by the shell and a relative high dielectric constant at room temperature and a low TCC at 125°C will be obtained. This can explain why the dielectric constant at room temperature increases while TCC at 125°C drops with increasing milling time.

4. Conclusions

The effects of milling process on the core-shell structures and the dielectric properties of BT-based X7R ceramic materials were investigated. As the milling time increases, the dielectric constant of the ceramics increases, whereas TCC at 125°C drops quickly, which mainly results from the changes in the core-shell structures.

The milling process has an important influence on the microstructure evolutions of the ceramics, which makes it easier for the additives to diffuse into BT particles by increasing the surface defects of BT particles. TEM micrographs and EDS results show that as the milling time extended, the grain shell gets thicker, the grain core gets smaller, whereas the chemical inhomogeneity between grain core and grain shell becomes weaker. There is an optimum milling time for the temperature-stable ceramics.

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