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Effects of MgO coating on microstructure and dielectric properties of $BaTiO_3$

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Abstract

Effects of MgO coating on microstructure and dielectric properties of $BaTiO_3$ have been studied compared with mechanically MgO mixed $BaTiO_3$. MgO-coated $BaTiO_3$ particles were prepared by a homogeneous precipitation method using $MgCl_2 \cdot 6H_2O$ and urea. TEM micrograph showed homogeneous adsorption of MgO particles on the $BaTiO_3$ surfaces. MgO coated and mixed samples showed different dielectric behaviors because uniformity of microstructures and shape of core-shell structure were different each other. Bulk density was slightly decreased with increasing MgO content. EPMA analysis indicates that microstructures and dielectric behaviors were affected by the distribution of MgO in the $BaTiO_3$ matrix.

Keywords: $BaTiO_3$; Coating; Dielectric properties; Mixing; MgO

1. Introduction

Magnesium oxide is one of the basic doping materials in $BaTiO_3$-based multilayer ceramic capacitors (MLCCs). Moreover, MgO together with rare earth oxides are widely used to achieve an X7R specification (X7R: the dielectric constant value at 25 °C changes by not more than ±15% in the temperature range from −55 to 125 °C) with a core-shell structure.[1–4] Mg ion is known to be substituted for Ti site in $BaTiO_3$ system and also reported to play an important role in inhibiting the grain growth of $BaTiO_3$.[5–7] Numerous works have been conducted to confirm the co-doping effects of rare earth oxides on the microstructure and electrical properties of $BaTiO_3$–MgO-based system.[3–7] However, there are only few works concerned with the properties of MgO singly doped $BaTiO_3$ system.[8–11]

Core-shell microstructures are usually obtained by admixing small amounts of several oxide additives to $BaTiO_3$ powders. Currently, oxide additives are mechanically mixed with the $BaTiO_3$ powder, but the distribution of additives in $BaTiO_3$ powders becomes critical since the additives are coarse and very small in amount. As the $BaTiO_3$ particle size is getting smaller, the uniform distribution of additives is more difficult. Therefore, various chemical techniques such as sol–gel,[12,13] heterocoagulation[14–16] and homogeneous precipitation coating[17,18] have been proposed to maximize the homogeneous distribution of additives.

In this study, the microstructure and dielectric properties of MgO-coated $BaTiO_3$ through the precipitation coating were studied and compared with those prepared by a conventional mixing method.

2. Experimental procedure

$BaTiO_3$ (Sakai BT-04) mixed with reagent grade MgO was prepared by a conventional ceramic processing technique. The ingredient raw materials were mixed in a ball mill and then dried in an oven. The amount of MgO addition was 0.5, 1.0, 2.0 and 3.0 mol%. MgO-coated $BaTiO_3$ with the same composition as those mixed ones was prepared by a homogeneous precipitation method using reagent grade $MgCl_2 \cdot 6H_2O$, and urea (NH_2CONH_2). All solutions and suspensions were prepared in aqueous solution. $BaTiO_3$ particles were suspended in distilled water and Mg solutions were added to the suspension with 1 M concentration urea and dispersant. The suspension system was magnetically stirred at room temperature and 80 °C for 1 and 2 h, respectively. After stirring, the dispersion was aged at 90 °C for 12 h and calcination was conducted at 700 °C. The powders were pulverized into fine particles and formed into a disk shape under a uniaxial pressure of 200 MPa. The specimens

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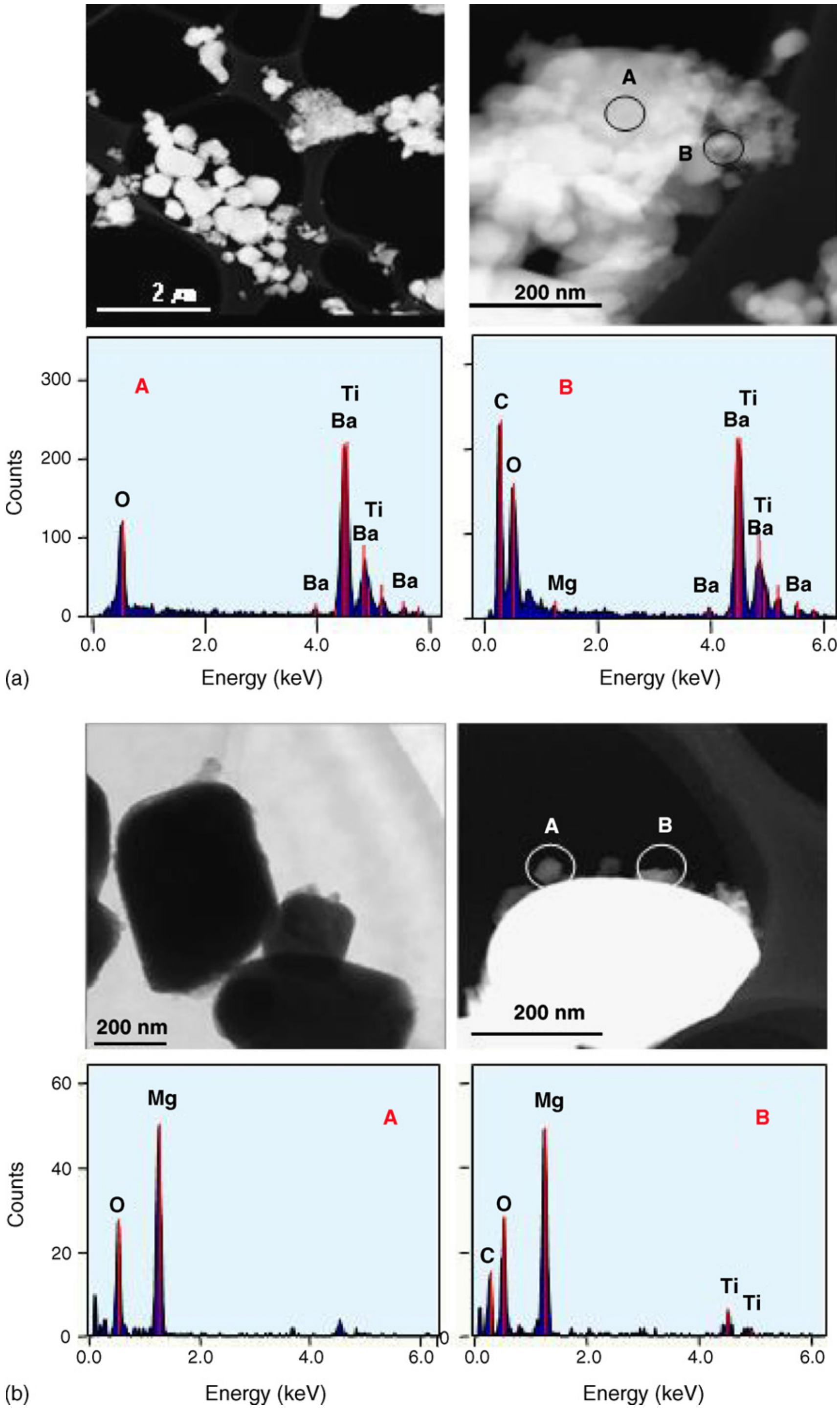

Fig. 1. TEM images and EDS analysis of 3.0 mol% MgO doped $BaTiO_3$ powder. (a) MgO mixing, (b) MgO coating.

were then sintered at 1320 °C for 2 h in air. Powder morphology and core-shell structure were characterized by a transmission electron microscopy with energy dispersive spectroscope (TEM, Jeol-300 kV). The dielectric constant was measured over a temperature range from −55 to 150 °C using the capacitance measurement system (Saunders & Associate) with an LCR meter (HP4284A). Thermally etched surfaces of sintered specimens were investigated using a scanning electron microscope (SEM, Hitachi- S2150). X-ray diffraction patterns were obtained using an automated diffractometer (Rigaku Rotaflex D/MAX System) with CuKα radiation.

3. Results and discussion

Fig. 1 shows TEM image of MgO mixed and coated $BaTiO_3$ and chemistry of specified areas by energy dispersive spectroscopy (EDS). MgO-coated $BaTiO_3$ powder confirmed that $BaTiO_3$ surface was covered with MgO particles, whereas MgO

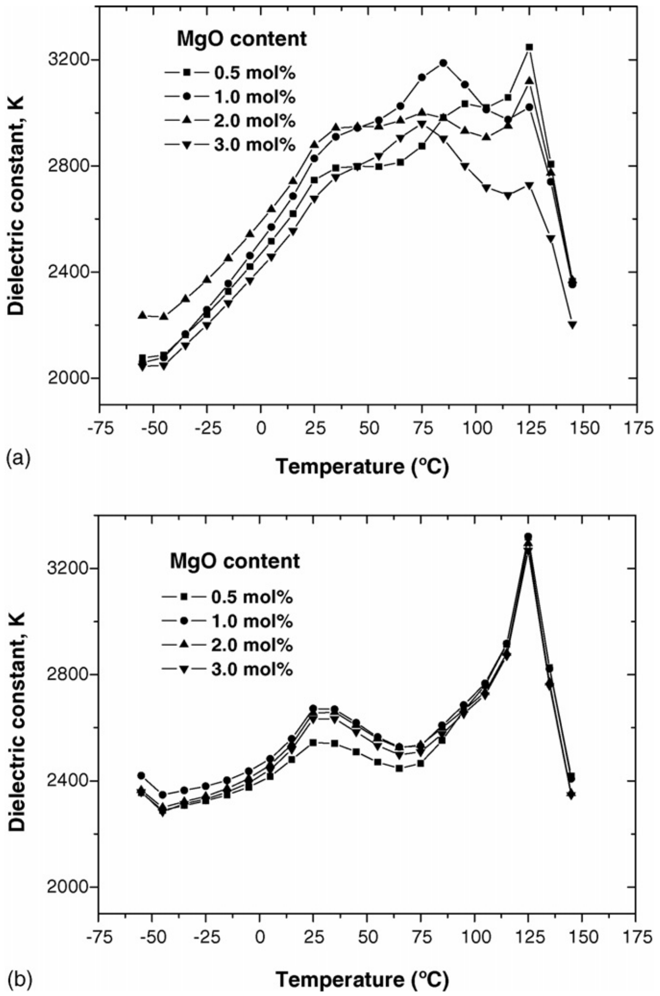

Fig. 2. Dielectric constants of MgO-doped $BaTiO_3$ with various MgO contents. (a) MgO mixing, (b) MgO coating.

mixed $BaTiO_3$ included inhomogeneous distributions of MgO. This uniform coating of MgO on $BaTiO_3$ could be caused by decomposition of urea and surface reaction between $BaTiO_3$ and MgO precursor.

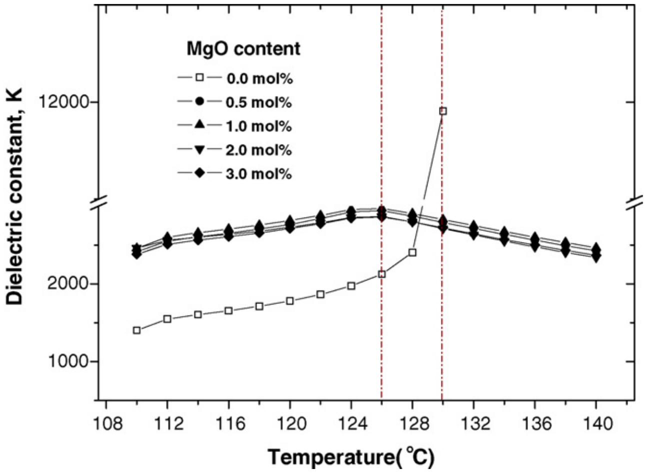

Fig. 3. Dielectric constants of MgO-coated $BaTiO_3$ with various MgO contents.

Urea is hydrolyzed according to the following reaction:[19]

$$(NH_2)_2CO + 3H_2O \rightarrow CO_2 + 2NH_3 + 2H_2O \qquad (1)$$

The decomposition of urea on the heating of solution released ammonia and carbon dioxide. Ammonium ions gradually and uniformly increase pH of the solution and induce the precipitation of Mg hydroxides. The precursor of magnesium hydroxide would be precipitated through the hydrolysis reaction of urea, the uniform precipitation of Mg precursors in the presence of $BaTiO_3$ particles leading to the hetero-coagulation which produced homogeneous distribution of MgO particles on the $BaTiO_3$ surface.

Fig. 2 shows the changes in dielectric constants of MgO mixed and coated $BaTiO_3$ as a function of MgO content over the temperature range from −55 to 150 °C. A significant difference was observed in dielectric behaviors between MgO mixed and coated samples although the maximum dielectric constants of both specimens were about 3200. In the case of MgO mixed specimen, the dielectric constant at the Curie temperature was decreased with increasing MgO content, but any consistent tendency was not observed between the Curie temperatures and

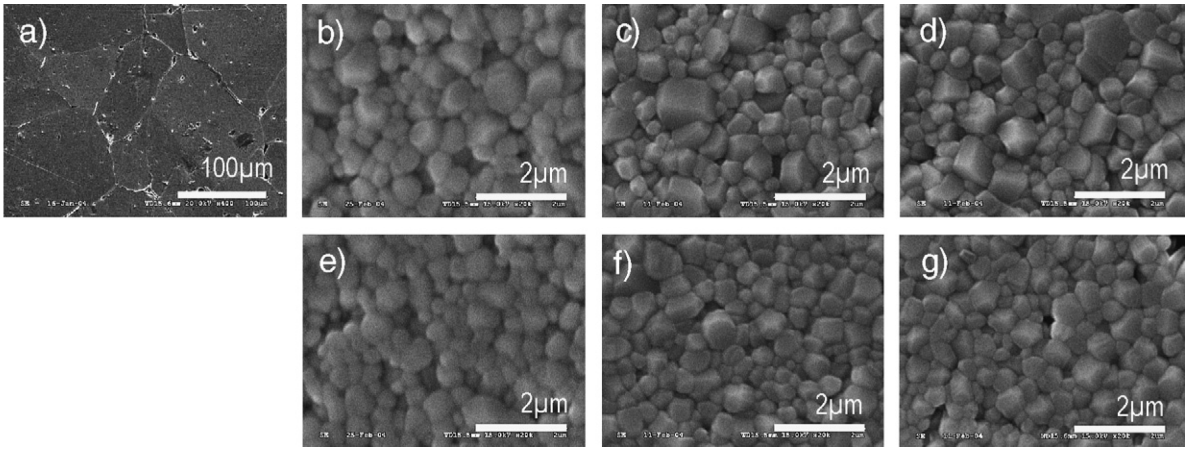

Fig. 4. Microstructures of MgO mixed (b–d) and coated (e–g) $BaTiO_3$ with various MgO contents sintered at 1320 °C. (a) 0.0 mol%, (b, e) 0.5 mol%, (c, f) 1.0 mol% and (d, g) 3.0 mol%.

MgO contents. In contrast with the MgO mixed case, dielectric behaviors of MgO-coated specimens were quite similar to each other over the temperature range measured only except that dielectric constants of the specimens with greater than 0.5 mol% MgO were slightly higher than that of 0.5 mol% MgO sample around room temperature. Plessner et al.[8] studied the effect of magnesia on $BaTiO_3$ permittivity that the Curie temperature shifted to lower temperatures by addition of 3.0 mol% MgO ($\Delta T_C = -50\,^\circ C$), whereas Baxter et al.[9] reported that the temperature of the cubic-tetragonal phase transformation was changed slightly upon MgO addition, $\Delta T_C = -3\,^\circ C$ for 3 mol% MgO. These controversial results are due to the difference in MgO dispersion degree which depends on experimental procedure. However, it is difficult to compare exactly two results because a full explanation for mixing process in their experiments was not given.

Fig. 3 shows dielectric constants of MgO-coated $BaTiO_3$ with various MgO contents over the temperature range from 110 to 140 °C. The Curie temperature of un-doped $BaTiO_3$ was observed at 130 °C and those of MgO coated specimens were observed at 126 °C regardless of MgO contents. This result is similar to the studies of MgO-doped $BaTiO_3$ by Baxter.[9] It was also confirmed that MgO additions effectively suppress the dielectric constants at the Curie temperature, which could make MgO an essential additive to stabilize TCC curves in X7R type MLCC manufacturing.

Fig. 4 shows microstructures of MgO mixed and coated samples with various MgO contents. The samples doped with MgO showed small grain sizes about 1 μm, whereas un-doped $BaTiO_3$ exhibited larger grain sizes (∼50 μm). Sakabe et al. reported that MgO was detected in the grain boundary region of $(Ba_{1-x}Ca_x)_m TiO_3$–MgO–SiO_2, which might act as a grain growth inhibitor.[20] Thus, small grain size in MgO–$BaTiO_3$ system might be due to barriers such as the secondary phases or the excess MgO existing in the grain boundary. The second phases related to MgO were not detected in the XRD profile of the specimens because the amount of excess MgO was too small to be detected by XRD analysis. Microstructures of MgO mixed specimens were less uniform than coated ones with an irregular shape of grains. The difference in microstructures between MgO mixed and coated specimens could be responsible for dielectric properties shown in Fig. 2.

Temperature characteristics of dielectric constants depend on metastable grain core-shell structures.[21,22] The grain core indicates the center region of the grain, representing the ferroelectric domain structure, and the grain shell is the outer region having a concentration gradient of additive oxides from the grain boundary toward the grain core. To explain the dielectric properties of the mixed composite, several models have been proposed and investigated.[22–24] The average dielectric constant is written by Lichtenecker's equation:[22]

$$\log K = V_c \log K_c + V_s \log K_s \qquad (2)$$

where K_c and K_s represent the dielectric constants of the core (undoped $BaTiO_3$) and shell (MgO doped) phase respectively, V_c and V_s are the volume fractions of core and shell phase. It is assumed that mixed MgO could not homogeneously disperse in $BaTiO_3$ so that the quantity of grains composed of core-shell structure was limited. On the contrary, it is obvious that MgO-coated $BaTiO_3$ have thinner and more homogeneous shell structure than MgO mixed $BaTiO_3$ in each grain because MgO was distributed uniformly in $BaTiO_3$ grain boundaries. Thus, MgO-coated specimens show higher dielectric constants at the Curie temperature of inherent ferroelectric $BaTiO_3$, whereas MgO mixed specimens exhibit higher dielectric constants between 60 and 80 °C due to the inhomogeneous core-shell structures. The inhomogeneous distribution of MgO leads to a substantially localized penetration of Mg ions into the core area, resulting in

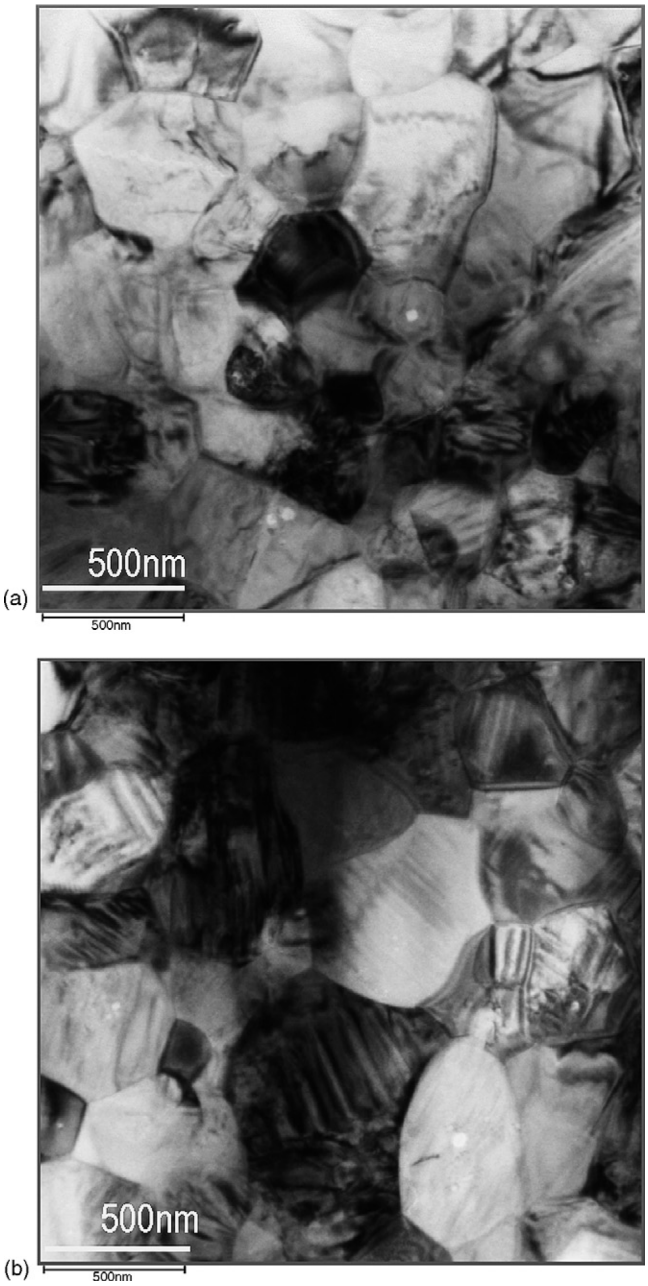

Fig. 5. TEM images of 3.0 mol% MgO-doped $BaTiO_3$ samples sintered at 1320 °C. (a) MgO mixing, (b) MgO coating.

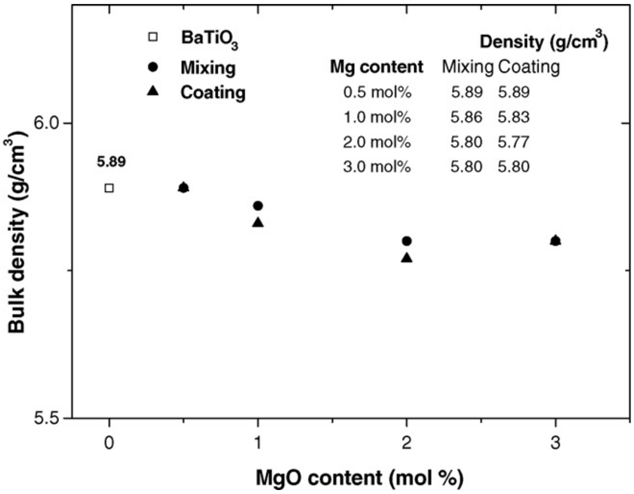

Fig. 6. Apparent density of MgO-doped $BaTiO_3$ as a function of various MgO contents.

the heavily MgO-doped shell structure and the shift of Curie point to lower temperatures.

Fig. 5 shows TEM images of 3.0 mol% MgO coated and mixed $BaTiO_3$ samples after sintering. Core-shell structure of MgO-coated specimen looks more obvious than that of mixed sample, and the MgO-coated sample exhibits homogeneous and narrow shell regions. This result is compatible with the dielectric behaviors shown in Fig. 2.

Fig. 6 shows bulk density of the MgO mixed and coated samples as a function of MgO content. The density of both mixed and coated specimens was decreased with increasing MgO contents. This is similar to the previous study of MgO doped $BaTiO_3$.[25] Excess MgO is assumed to exist in the grain boundary region and suppresses the grain growth, resulting in poor densification. Fig. 7 shows EPMA analysis of 3.0 mol% MgO mixed and coated samples after binder burned out. Localized bright areas with high concentration of MgO were observed in the mixed sample, whereas MgO was homogeneously distributed in the coated sample. This result implies that the inhomogeneous presence of MgO in the mixed sample gave rise to the irregular core-shell shape and microstructure.

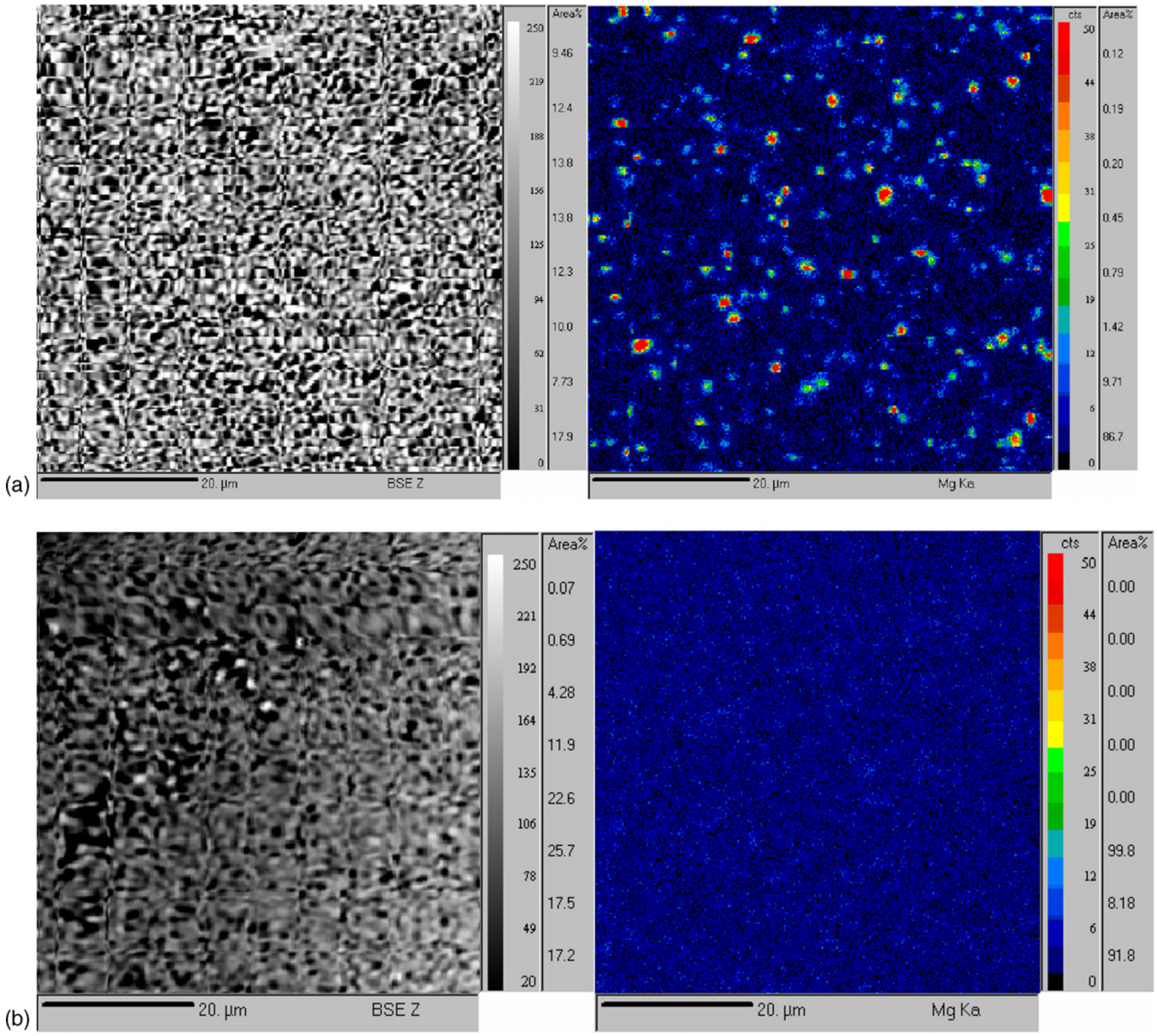

Fig. 7. EPMA analysis of 3.0 mol% MgO-doped $BaTiO_3$ after binder burned out (a) MgO mixing, (b) MgO coating.

4. Conclusions

MgO-coated $BaTiO_3$ particle was prepared from $BaTiO_3$ powders and $MgCl_2{\cdot}6H_2O$ by a homogeneous precipitation method using urea. MgO mixed and coated sample gave different dielectric behaviors at the same MgO content and sintering condition. The different physical properties are due to MgO distribution, leading to the different microstructure and core-shell structure. The inhomogeneous distribution of MgO leads to a substantially localized penetration of Mg ions into the core area, resulting in the heavily MgO-doped shell structure and the shift of Curie point to lower temperatures. Coating method can effectively improve the distribution of MgO in $BaTiO_3$ matrix and provide homogeneous microstructures.

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