

Electrical properties of MLCCs of Mg/Dy/Si oxides coated BaTiO₃ particles prepared by thermal hydrolysis method

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To improve the electrical properties of multilayer ceramic capacitors, triple (Mg/Dy/Si) oxides coating on the surfaces of 150-nm BaTiO₃ (BT) particles was conducted by using the thermal hydrolysis method. Multi-layer (5 layers) ceramic capacitors (MLCCs) of triple oxides coated BT (TOBT) particles were obtained by using green sheet process and their electrical properties were measured. The MLCCs of TOBT particles gave a better stable dielectric constant and dissipation factor for the sintering temperature compared with those of the reference specimen prepared by using mixing process. In addition, a stable temperature coefficient of capacitance (TCC) was obtained. The morphology and homogeneity of TOBT particles were measured by using scanning transmission electron microscope-high angle annular dark field (STEM-HAADF) and energy dispersive X-ray spectroscopy (EDX).

Key words: Thermal hydrolysis, SiO₂, MgO, Dy₂O₃, BaTiO₃, Multi layer, MLCC properties.

Introduction

BaTiO₃ (BT) has been an excellent dielectric material for multi-layer ceramic capacitors (MLCCs). MLCCs are composed of multi-layer ceramic sheets produced by using green sheet technology. Recently, the reduction of thickness in multi-layer ceramic sheets is an important issue since the miniaturization of electronic components has been greatly required. Nano-sized BT particles of ≈ 150 nm have been utilized to reduce the thickness of multi-layer ceramic sheets. However, the grain growth of BT particles has been observed during the sintering process. As a result, electrical stability and reliability problems have occurred in MLCCs.

To improve above mentioned problems, the addition of a rare-earth element such as Dy [1-2], Y [3], or Er [4] has been examined. Rare-earth elements together with Mg are well known to stabilize the dielectric constant in the sintering temperature and decrease the dissipation factor [5-6] since rare-earth elements with Mg readily cause the formation of a core-shell structure [7]. However, a uniform dispersion of additives is difficult to achieve using the mixing process with the addition of a small amount of oxides. In addition, the grain growth of BT particles at the sintering temperatures from 1130 to 1170 °C has consequentially not been able to be controlled.

To improve above mentioned problems, a thermal hydrolysis coating method [8-9] has been applied. This method can easily control the coating conditions as a function of pH and thermal treatment of low temperature. Also, the control of grain growth is preferable to the mixing process since the initial BT particles are coated with a small amount of oxides before sintering.

In this paper, triple (Mg/Dy/Si) and double (Mg/Dy) oxides were coated on BT (TOBT and DOBT) particles by using the thermal hydrolysis method and the electrical properties of MLCCs were measured to confirm their stability.

Experimental

150-nm BT particles (Kyoritsu, Japan) were used as a core material and DyCl₃ (Aldrich), MgCl₂ (Aldrich), and Na₂OSiO₂ (Aldrich) compounds were used as coating (shell) materials. The composition ratio of coating materials was 1.25 mol (Si) : 0.65 mol (Dy) : 1.02 mol (Mg). In this experiment, double oxides coating (Mg/Dy) and triple oxides coating (Mg/Dy/Si) onto BT particles were conducted. The mixing process of MgO (1.02 mol, Ube materials), Dy₂O₃ (0.65 mol, shinetsu), and SiO₂ (1.25 mol, AEROSIL) powders by conventional process was also selected to compare the coating process.

The mixing process was as follows;

The BT powders were ball-milled in dispersant, and ethanol, and toluene solvents for 5 hrs. After the oxide materials were added and mixed with the BT powder,

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the binder (BM-2) was mixed in the powders for 15 hrs.

The triple oxides coating process was as follows. 100g of BT particles were mixed into 2 L of diluted water and heated to 80 °C (called as slurry 1). NaOH solution was added to heated slurry 1 to increase the pH, and Na₂OSiO₂ was added to prepare the SiO₂ coating (called as slurry 2). The pH of slurry 2 changed with the addition of Na₂OSiO₂.

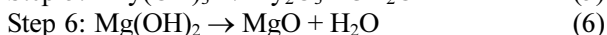
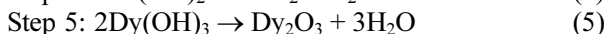
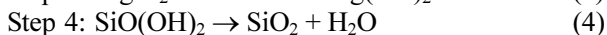
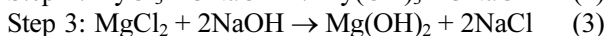
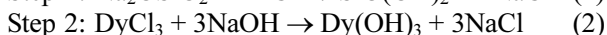
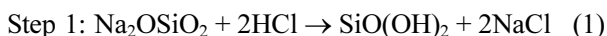
Step 1: Therefore, HCl was cyclically added to maintain the pH between 6 and 8 (called as slurry 3).

Step 2: DyCl₃ and NaOH solutions were added and mixed into slurry 3 (called as slurry 4) to coat the Dy oxide.

Step 3: MgCl₂ and NaOH solutions were added and mixed into slurry 4 to obtain the MgO coating (called as slurry 5). The obtained slurry 5 was mixed for 30min and washed in diluted water.

Steps 4, 5, and 6: The washed slurry 5 was dried at 125 °C for 10 hrs, and fired at 650 °C for 30 min in air.

The reaction process is summarized as follows;

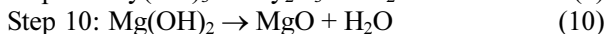
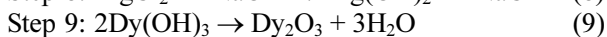
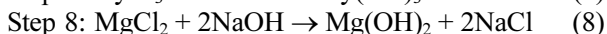
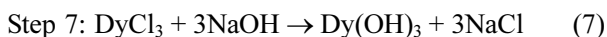


The double oxides coating process was similar to the triple oxides coating process. 100 g of BT particles were mixed into 2 L of diluted water and heated to 80 °C (slurry 6).

Step 7: DyCl₃ and NaOH solutions were added and mixed into mixed slurry 6 to coat the Dy oxide (slurry 7).

Step 8: MgCl₂ and NaOH solutions were added and mixed into slurry 7 to obtain the MgO coating (slurry 8). The obtained slurry 8 was mixed for 30 min and washed in diluted water.

Steps 9 and 10: The washed slurry 8 was dried at 125 °C for 10hrs, and fired at 650°C for 30 min in air.



Doctor blade casting was conducted to obtain the green sheets (5 sheets) of powder slurry. The obtained sheets were laminated, pressed and cut to a 1 mm thickness. The cut sheets were baked at 300 °C to remove the binder and then sintered at 1130, 1150, and 1170 °C for 3 hrs in air atmosphere (called as specimens).

The amount of each element was analyzed by inductively coupled plasma (ICP). TEM (FEI G2 F20) analysis with EDX was performed at 200kV to observe the coated BT particles and the composition profiles of

the additives. The density of specimens was measured by using the Archimedes method. The resistivity of specimens was measured by Agilent 4339B (Agilent) at a condition of 250V, 5 mA, and 60s. The dielectric constant and dissipation factor of specimens were measured by using 4284A precision LCR meter (Hewlett-Packard Co.) at the condition of 1 Vrms and 1 kHz. In addition, the TCC of specimens was also measured by using 4284A precision LCR meter (Hewlett-Packard Co.) in the temperature range of -55 to 135 °C at 1 kHz and 1 Vrms.

Results and Discussion

As shown in Table 1, it was confirmed that the BT particles with double oxides and triple oxides contained two (Mg and Dy) and three (Si, Mg and Dy) elements, respectively. The double oxides coated BT (DOBT) particles contained the Mg (1.17 mol) and Dy (0.75 mol) elements, and the triple oxides coated BT (TOBT) particles contained the Si (1.14 mol), Mg (1.18 mol), and Dy (0.73 mol) elements. From ICP analysis, the amount of additives of the coated samples was almost the same as that of the initial prepared amounts (Si: 1.25 mol, Dy: 0.65 mol and Mg: 1.02 mol).

Fig. 1 shows the TEM image and EDX analysis of the DOBT (a) and TOBT (b) particles. As shown in Fig. 1(a), two types of elements of Dy and Mg were detected in the DOBT particles by point analysis. In addition, the Dy element was homogeneously distributed on the BT particle by using line scan analysis. As shown in fig. 1(b), two types of elements (Dy and Si) were detected in the TOBT particles by using point analysis. In the line scan analysis, it was confirmed that two elements (Dy and Si) were homogeneously distributed on the surface of the BT particles. From these results, it could be expected that the core-shell structure was formed in the DOBT and TOBT particles. Coating of the Mg element could not be detected by EDX analysis due to the detection sensitivity.

Fig. 2 shows the density of specimens as a function of sintering temperature. The density of the reference and TOBT specimens slowly increased from 5.73 to 5.97 and from 5.81 to 5.93 g/cm³ with the increase of sintering temperature from 1130 to 1170 °C, respectively. The density of the DOBT specimens rapidly increased

Table 1. ICP analysis of coated particles.

Metal element	Double oxides coated BT particle	Triple oxides coated BT particle
Dy	4596 ppm (0.75 mol)	4426 ppm (0.73 mol)
Mg	1045 ppm (1.17 mol)	1055 ppm (1.18 mol)
Si	94 ppm (0.09 mol)	1212 ppm (1.14 mol)

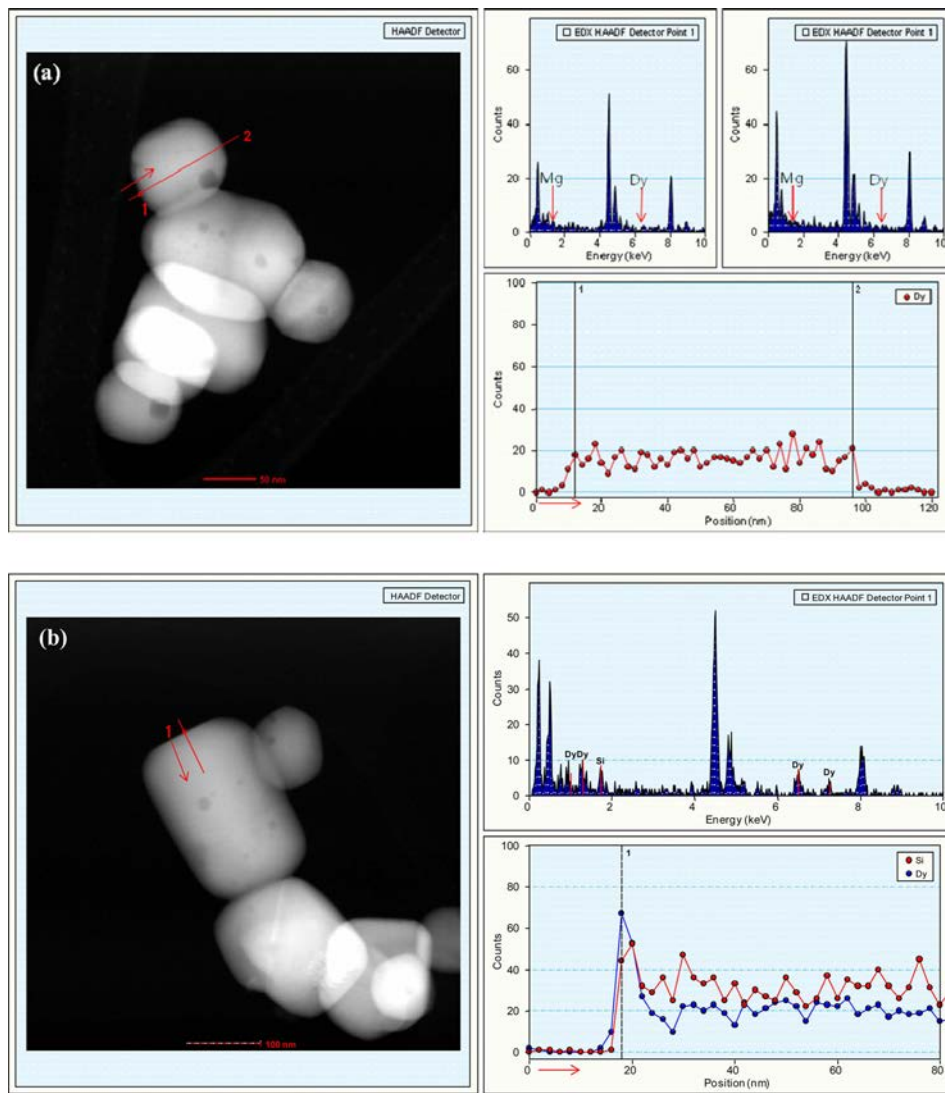


Fig. 1. STEM-HAADF and EDX (point and line scan) analysis; (a) DOBT particles, (b) TOBT particles.

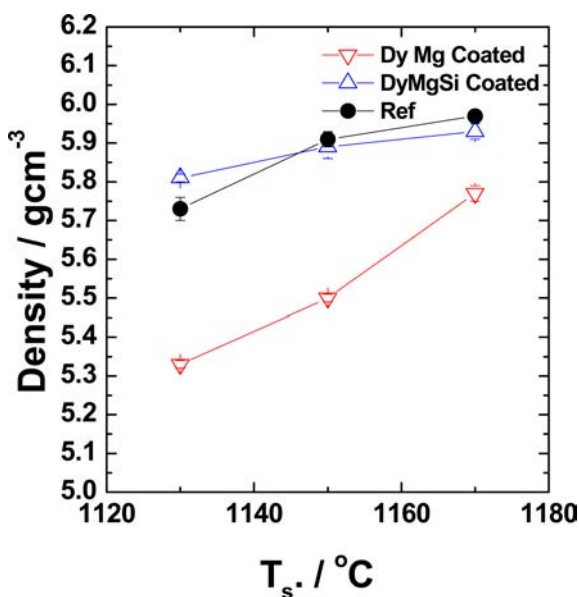


Fig. 2. Density of the mixed and coated BT specimens at the sintering temperature.

from 5.33 to 5.77 g/cm³ with the increase of temperature. From this result, it could be verified that the reference and TOBT specimens had much higher density than the DOBT specimen at low sintering temperature due to the effect of SiO₂ addition [9–11].

Fig. 3 shows the resistivity of specimens as a function of sintering temperature. The reference and TOBT specimens showed a slight change (12.13 to 12.61 Ωcm and 12.43 to 12.52 Ωcm). However, the DOBT specimens showed a large increase with the increase of temperature (9.42 to 12.74 Ωcm). The low resistivity of the DOBT specimens at 1130 and 1150 °C was accredited to the insufficient sintering due to the absence of SiO₂.

Fig. 4 shows the dielectric constant of specimens as a function of sintering temperature. The dielectric constant of the reference and TOBT specimens showed a value of over 2180, whereas the DOBT specimens significantly increased from 1670 to 2130 with the increase of sintering temperature due to the insufficient sintering. The dielectric constant deviation of the TOBT specimens (± 59) was lower and more stable

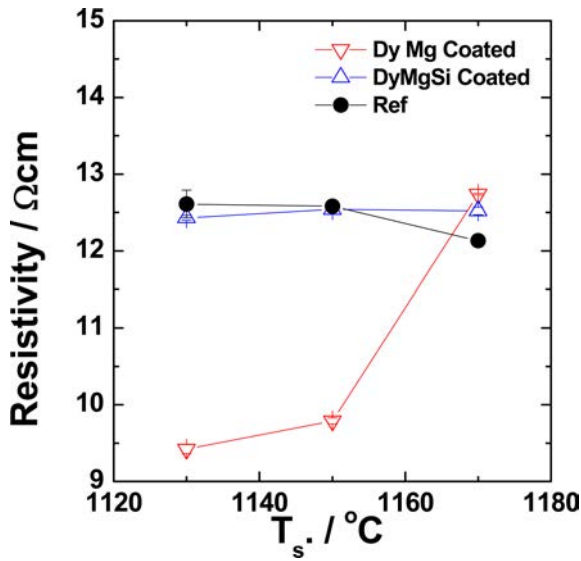


Fig. 3. Resistivity of the mixed and coated BT specimens at the sintering temperature.

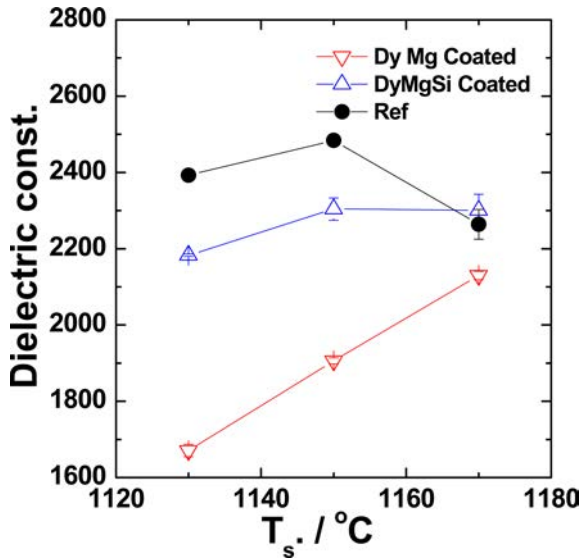


Fig. 4. Dielectric constant of the mixed and coated BT specimens at the sintering temperature.

than that of the reference specimens (± 110).

Fig. 5 shows the dissipation factor of specimens as a function of sintering temperature. For the reference and TOBT specimens, a dissipation factor of less than 1.43% was obtained, regardless of the change of sintering temperature. The dissipation factor of the DOBT specimens was dramatically decreased from 5.38% to 1.06% with the increase of temperature from 1130 to 1170 °C. This phenomenon also resulted from the insufficient sintering. Moreover, the dissipation factor deviation of the TOBT specimens ($\pm 0.05\%$) was lower and more stable than that of the reference specimens ($\pm 0.15\%$) with the change of sintering temperatures.

Fig. 6 shows the TCC of specimens as a function of sintering temperature. As shown in Fig. 6(a), the

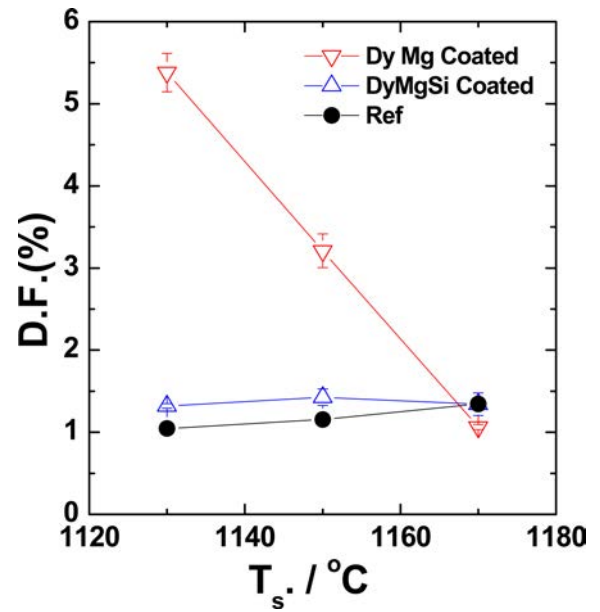


Fig. 5. Dissipation factor of the mixed and coated BT specimens at the sintering temperature.

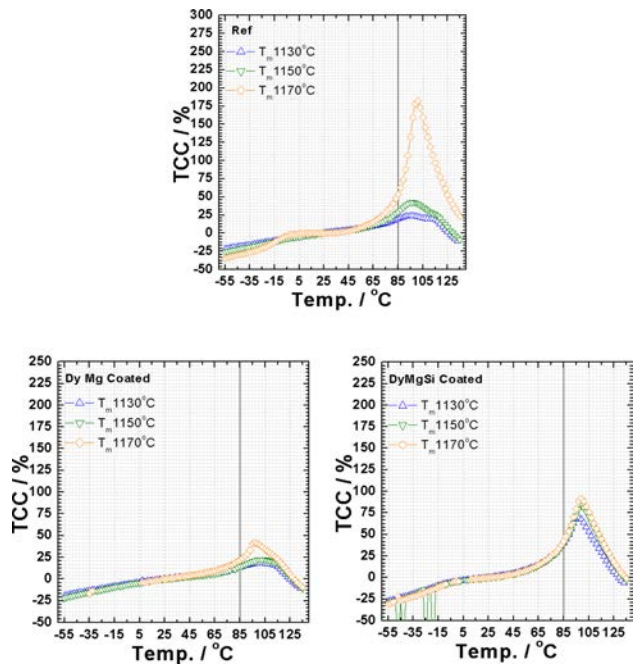


Fig. 6. TCC of the mixed and coated BT specimens at the sintering temperature; (a) reference, (b) DOBT, (c) TOBT.

maximum TCC of the reference specimens at 1130 and 1150 °C was under 40%, whereas the specimen at 1170 °C showed that of almost 180%, resulting in the grain growth of the BT particles [1]. The BT particles grew with the increase of sintering temperature since the additive oxides were not homogeneously dispersed due to the mixing process. Fig. 6(b) shows that the TCC of DOBT specimens was stable under 40%, regardless of the sintering temperature. The maximum TCC of the TOBT specimens (Fig. 6(c)) was from 70% (sintered at 1130 °C) to 90% (sintered at 1170 °C),

showing stable behavior. From this result, it was expected that the grain growth of the BT particles could be well controlled by the core-shell structure due to the homogeneous oxides coating on the BT particles.

Conclusions

Triple (Mg, Dy, and Si) and double (Mg and Dy) oxides coating on the surfaces of 150-nm BaTiO₃ particles were conducted by using the thermal hydrolysis method. The electrical properties of multi-layer (5 layers) ceramic capacitors (MLCCs) of TOBT particles were measured. The core-shell structure of the coated BT particles was expected by using TEM and EDX. The MLCCs of the TOBT particles gave a better stable dielectric constant and dissipation factor at a sintering temperature compared with those of the reference specimens prepared by using mixing process. In addition, a stable temperature coefficient of capacitance (TCC) was obtained.

Acknowledgments

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of

Education, Science and Technology (NRF-2013R 1A2 A2A01010027).

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