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Effect of Y_2O_3/MgO Co-doping on the electrical properties of base-metal-electroded $BaTiO_3$ materials

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Abstract

Effect of MgO and Y_2O_3 additions on modifying the dielectric constant-temperature (K–T curve) properties of the base-metal-electroded $BaTiO_3$ materials was systematically studied. The absolute value of $(\Delta C/C)_{-55\ ^\circ C}$ and $(\Delta C/C)_{125\ ^\circ C}$ can be reduced, i.e., be moved upward, by incorporating large enough concentration of MgO and Y_2O_3 additives into the $BaTiO_3$, such that the K–T characteristics of the materials meet the X7R specification. The Y_2O_3 doping is more effective than the MgO doping in moving the $(\Delta C/C)_{-55\ ^\circ C}$ and $(\Delta C/C)_{125\ ^\circ C}$ upward, which can be attributed to the fact that Y_2O_3 species addition flattens the K–T curves without shifting the Curie point of the materials. However, the proportion of Y_2O_3 incorporated into the materials should exceed the solubility of the $BaTiO_3$ materials such that the Y_2O_3 species can reside at the grain boundary region, forming a core-shell microstructure.

Keywords: Base-metal-electroded capacitor; $BaTiO_3$; X7R

1. Introduction

High performance and small sized multilayer ceramic capacitors (MLCC), which possess high reliability and are compatible with surface mounting technology, have a great potential for industrial applications.[1] Technology for MLCC mainly involves the co-firing of dielectrics and electrode materials (Ag/Pd alloy). However, utilization of large Pd content electrode materials increases the manufacturing cost tremendously. The development of inexpensive electrode materials such as base metals (Cu and Ni) is thus urgently needed for reducing the production cost for MLCC.[2,3] The base-metal-electroded (BME) capacitors need to be fired under reducing atmosphere, since the Cu (or Ni) metal is subjective to oxidation during sintering in air. Many approaches have been reported that are able to successfully maintain high insulation resistance of the $BaTiO_3$ materials, even when they were sintered in reducing atmosphere.[3–9] In X7R type MLCC, the key factor resulting in a low temperature coefficient of dielectric properties is presumed to be the presence of the core-shell microstructure,[10–12] which can be achieved by critically controlling the doping species and concentration.[13,14] However, how the dopants affect the microstructure and hence the related dielectric properties is still not yet fully understood.

In this paper, effect of Yttrium oxide, Y_2O_3, and Magnesium oxide, MgO, additions on the dielectric properties of the $BaTiO_3$ materials was systematically examined. The probable mechanism of the modification on the electrical properties of $BaTiO_3$ materials which resulted from the addition of these dopants was discussed.

2. Experimental

The commercial $BaTiO_3$ powders (0.5 μm) were mixed with the dopants, Y_2O_3 (0–2.0 mol%), MnO_2 (0.4 mol%), MgO (1–5 mol%), and sintering aid, $(Ba_{0.6}Ca_{0.4})SiO_3$ (3 mol%), and were pressed and then sintered at 1250–1300 °C for 3 h in 10^{-10} Torr Po_2 atmosphere, followed by re-oxidized at 1000 °C for 2 h in 80 ppm Po_2 atmosphere. The microstructures of the samples, which were polished and then chemically etched, were examined using scanning electron microscopy (SEM, Joel TSM-840 A).

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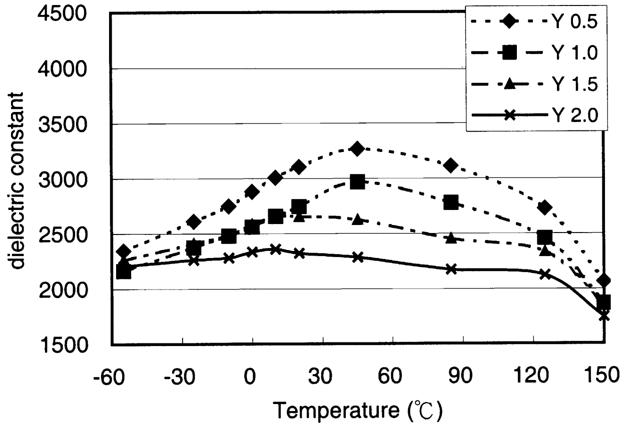
The Cu-paste was screen printed onto the sintered samples, followed by firing at 900 °C for 10 min in 30 ppm Po_2 to serve as electrodes. The dielectric properties of the capacitor materials were measured from −55 to 150° using HP 4278 capacitance meter. The insulation resistance (IR) of the samples was measured using HP 4339 impedance meter.

3. Results and discussion

The fine-grain $BaTiO_3$ materials containing only 1 mol% MgO dopants (no Y_2O_3) possess similar K–T dielectric properties as the conventional large-grain $BaTiO_3$ materials. Although the K–T peaks were markedly broadened due to the fine grain characteristics of the materials (not shown), the capacitance variation, $\Delta C/C=(C–C_{rt})/C_{rt}$, is still very large ($C$ and C_{rt} representing the capacitance values at measuring temperature and at room temperature, respectively). These samples are out of the range of X7R specification, which requires $\Delta C/C<\pm15\%$ in −55 to 125 °C temperature range.

Incorporation of Y_2O_3 species in MgO-containing samples influences the dielectric constant-temperature (K–T) properties profoundly. Fig. 1 shows the variation of K–T and $\Delta C/C$–T properties with concentration of Y_2O_3 (0.5–2 mol%) for the $BaTiO_3$ materials containing 1 mol% MgO. Fig. 1a (dotted curve) indicates that the K–T curves were flattened pronouncedly due to the addition of the Y_2O_3 dopants without markedly shifting the Curie point. The absolute value of $\Delta C/C$ decreases, i.e. the $\Delta C/C$ moves upward, as Y_2O_3 content increases, such that the samples containing Y_2O_3 larger than 1.5 mol% meet the X7R specification, which is encircled by a broad rectangular line in Fig. 1b. Similar phenomenon is observed for the 2 mol% MgO-incorporated materials. The K–T curves were even more pronounced by flattening, with the Curie temperature only slightly shifted, due to Y_2O_3 addition, such that it needs only to include 1 mol% Y_2O_3 to push the $BaTiO_3$ materials into X7R specification (Fig. 2a). For the samples containing

(a) K-T, MgO (1 mol. %)



(b) ΔC/C-T, MgO (1 mol.%)

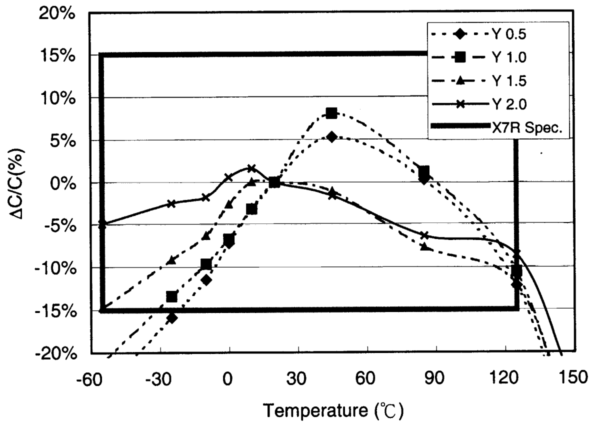
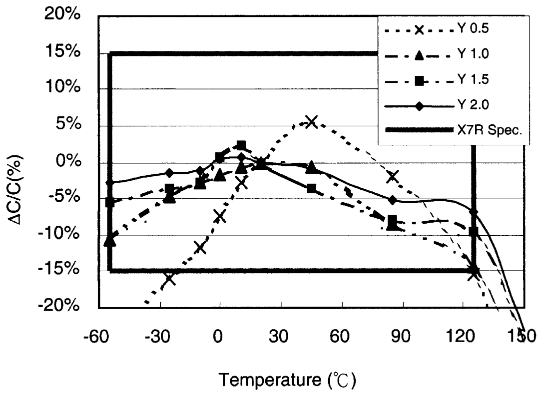


Fig. 1. Y_2O_3 effect on the (a) dielectric properties and (b) $\Delta C/C$ characteristics of 1250 °C-sintered $BaTiO_3$ materials, which are incorporated with 1.0 mol% MgO.

(a) 1250℃ sintered



(b) 1300℃ sintered

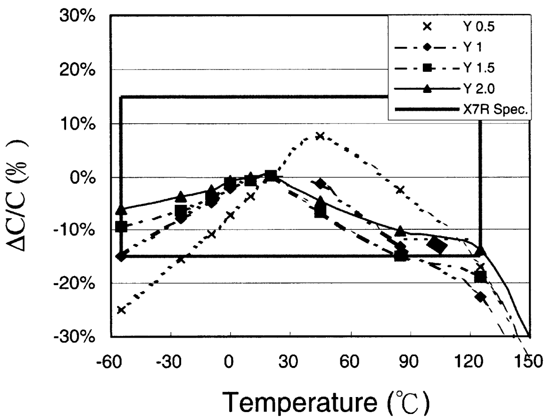
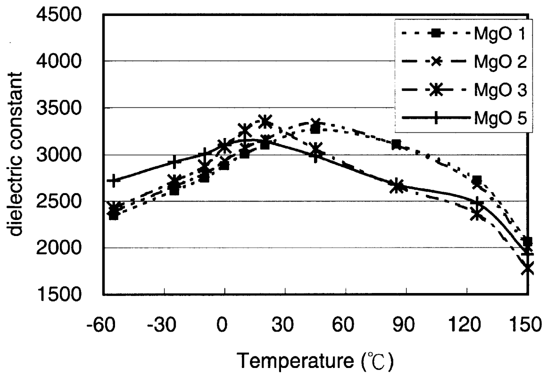


Fig. 2. Y_2O_3 effect on the $\Delta C/C$ characteristics of (a) 1250 °C and (b) 1300 °C sintered $BaTiO_3$ materials, which are incorporated with 2.0 mol% MgO.

3 mol% MgO, the $(\Delta C/C)_{125\,^{\circ}\mathrm{C}}$ became very large such that it needs larger amount of Y_2O_3 (1.5 mol%) to push the materials into X7R specification (not shown).

To understand why the 3 mol% MgO containing materials need larger proportion of Y_2O_3 dopants to reach the X7R specification, the effect of in MgO-addition was examined. Fig. 3a shows that for materials containing 0.5 mol% Y_2O_3, the Curie temperature is around 45 °C for the samples doped with 1 or 2 mol% MgO and shifts downward to around 20 °C for those doped with 3 mol% MgO. Increasing the MgO-content to 5 mol% shifts the Curie point further to a lower temperature. These results indicate that the increase in MgO-content increases the low temperature capacitance ($C_{-55\,^{\circ}\mathrm{C}}$), but reduces the high temperature capacitance ($C_{125\,^{\circ}\mathrm{C}}$), such that the $(\Delta C/C)_{125\,^{\circ}\mathrm{C}}$ moved downward away from the X7R specification, when the $(\Delta C/C)_{-55\,^{\circ}\mathrm{C}}$ moved upward into the X7R specification (Fig. 3b). A similar phenomenon was observed for 1 mol% Y_2O_3 -doped material (not shown), i.e., addition of MgO shifts the K-T curve without changing the shape, resulting in the increase in $C_{\text{-}55\,^{\circ}\mathrm{C}}$ and the decrease in $C_{125\,^{\circ}\mathrm{C}}$ such that the $(\Delta C/C)_{125\,^{\circ}\mathrm{C}}$ moved out of the X7R specification as MgO-content increased. In contrast, addition of Y_2O_3 species suppresses pronouncedly the maximum capacitance, with the low and high temperature capacitance ($C_{-55\,^{\circ}\mathrm{C}}$ and $C_{125\,^{\circ}\mathrm{C}}$) maintained essentially at the same value(cf Figs. 1b and 2a), such that both the $(\Delta C/C)_{-55\,^{\circ}\mathrm{C}}$ and $(\Delta C/C)_{125\,^{\circ}\mathrm{C}}$ move upward toward the X7R specification. Restated, the main difference between the effect of MgO and Y_2O_3 dopants on the K–T properties of $BaTiO_3$ materials is that the addition of MgO species shifts the K–T curves toward lower temperature without changing their shape, whereas the incorporation of Y_2O_3 species flattens the K–T curves without changing the Curie point.

(a) K-T, Y_2O_3 (0.5 mol.%)



(b) ΔC/C-T, Y_2O_3 (0.5 mol.%)

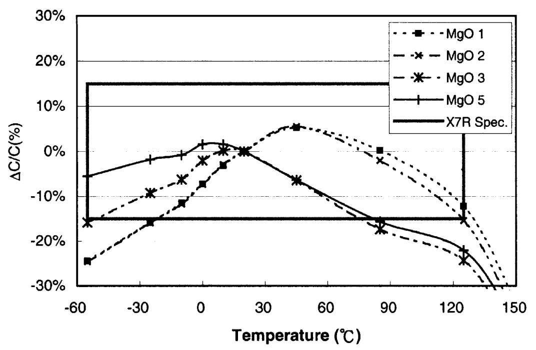


Fig. 3. MgO effect on the (a) dielectric constant and (b) $\Delta C/C$ properties of 1250 °C-sintered $BaTiO_3$ materials, which are incorporated with 0.5 mol% Y_2O_3.

The above described results indicate that co-doping a sufficient amount of MgO and Y_2O_3 species is essential in order to shift both of the $(\Delta C/C)_{-55\,^{\circ}\mathrm{C}}$ and $(\Delta C/C)_{125\,^{\circ}\mathrm{C}}$ of $BaTiO_3$ materials upward into the X7R specification. Y_2O_3 species more efficiently move the K-T behavior into the X7R specification owing to the fact that these species lowered the maximum capacitance ($C_{\max}$) value without shifting the Curie temperature. However, such an effect was observed only when the materials were sintered at 1250 °C (3 h). Increasing the sintering temperature further to 1300 °C (3 h) will change the behavior of Y_2O_3 dopants, which is illustrated in Fig. 2b. For $BaTiO_3$ materials containing 2 mol% MgO, the addition of small amount of Y_2O_3 (<1.5 mol%) moved the $(\Delta C/C)_{125\,^{\circ}\mathrm{C}}$ away from X7R specification, although the $(\Delta C/C)_{\circ 55\,^{\circ}\mathrm{C}}$ was shifted into this specification. Only when more than 2 mol% Y_2O_3 was incorporated, both the $(\Delta C/C)_{-55\,^{\circ}\mathrm{C}}$ and $(\Delta C/C)_{125\,^{\circ}\mathrm{C}}$ can be shifted toward the X7R specification. These results imply that addition of small amount of Y_2O_3 only shifts the K–T curve without changing the shape. The K–T curve can be flattened without moving the Curie temperature only when the proportion of Y_2O_3 incorporated is larger than 2 mol%.

It should be noted that the 1250 °C-sintered materials need only 1 mol% Y_2O_3 (and 2 mol% MgO) to move the K–T curves of the materials into X7R specification (cf. Fig. 2a). In contrast, the 1300 °C-sintered ones require at least 2 mol% Y_2O_3, in addition to and 2mol% MgO to result in the same effect (cf. Fig. 2b). Restated, larger proportion of Y_2O_3 is needed for 1300 °C-sintered samples to flatten the K–T curve without shifting T_C. To understand such a phenomenon the evolution of the microstructure with sintering temperature for MgO and Y_2O_3 co-doped samples were examined. SEM micrographs for the $BaTiO_3$ (2 mol% MgO) materials containing 0.5 or 1.5 mol% Y_2O_3, which were sintered at 1250 and 1300 °C for 3 h. are shown in Fig. 4a and b, respectively. These figures indicate that, when sintered at 1250 °C (3 h), large grains (around 0.6 μm) coexist with the fine grain (around 0.2 μm) for the samples incorporated with small proportion of Y_2O_3 ($\leqslant 0.5$ mol%, micrograph a_{I}). The grains are uniformly small ($\sim$0.2μm), for those containing a large proportion of Y_2O_3 (1.5 mol%, micrograph a_{II}). Increasing the

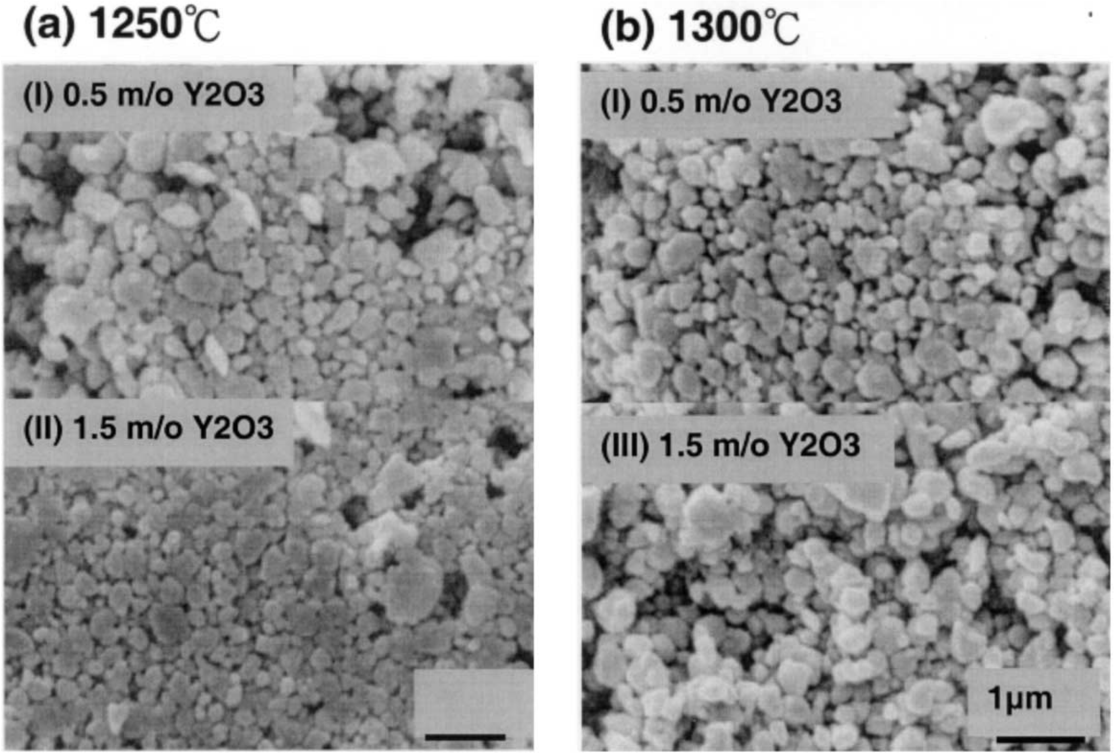


Fig. 4. SEM microstructure of (a) 1250 °C and (b) 1300 °C sintered $BaTiO_3$ materials, which are simultaneously incorporated with 0.5 or 1.5 mol% Y_2O_3 and 2 mol% MgO.

sintering temperature from 1250 to 1300 °C resulted in the presence of large grains, even for the samples containing 1.5 mol% Y_2O_3 (micrograph b_I and b_{II}). It needs at least 2 mol% Y_2O_3 to suppress the grain growth phenomenon (no shown). Such a phenomenon implies that the first few percent of Y_2O_3 added could be dissolved into the $BaTiO_3$ matrix, shifting the K–T curves pronouncedly, when sintered at too high temperature. Only when the amount of Y_2O_3 added is larger than the solubility of the $BaTiO_3$ materials, will the Y_2O_3 species reside at the grain boundary region, such that the K–T curves of the $BaTiO_3$ matrix were be flattened without shifting the Curie temperature, converting the $BaTiO_3$ into X7R type material.

4. Conclusion

Effect of MgO and Y_2O_3 additions were observed to markedly modify the dielectric constant-temperature (K–T curve) properties of the $BaTiO_3$ materials. Y_2O_3 doping can simultaneously reduce the absolute values of the $(\Delta C/C)_{-55\ °C}$ and $(\Delta C/C)_{125\ °C}$ such that the K–T characteristics of the materials moved toward the X7R specification. In contrast, the MgO doping shifted the T_C without altering the shape of K–T curves such that the $(\Delta C/C)_{-55\ °C}$ moved upward but the $(\Delta C/C)_{125\ °C}$ moved downward and the materials moved away from the X7R specification. However, the proportion of Y_2O_3 incorporated into the materials should exceed the solubility of the $BaTiO_3$ such that the Y_2O_3 can reside at the grain boundary region, forming a core-shell microstructure.

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