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Microstructures of X7R type base-metal-electroded $BaTiO_3$ capacitor materials prepared by duplex-structured process

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Abstract

Low temperature coefficient of capacitance (TCC) for the MgO/Y_2O_3 co-doped $BaTiO_3$ materials can be achieved by a duplex-structured process. The results of structure refinement reveal that large amount of MgO species can not only suppress the grain growth but increase the volume fraction of cubic phase of paraelectric $BaTiO_3$ at room temperature. Investigations of transmission electron microscopy (TEM) indicate that the detailed microstructure is extremely complicated for the $BaTiO_3$ materials. The heavily doped constituents of the samples remained as fine grains with paraelectric phase, whereas the lightly doped constituents of the materials grew, resulting in a core-shell microstructure via the incorporation of the MgO species when the mixture of the two constituents was sintered. The unique dielectric constant (*K*)–temperature (*T*) characteristics of the samples are ascribed to the duplex structure of the samples, which contain fine grains of cubic structure and large grains of core-shell structure.

Keywords: Electron microscopy; $BaTiO_3$; Capacitors

1. Introduction

Multilayer ceramic capacitors (MLCCs) are becoming more widely used in electronic circuits, especially with the trend toward miniaturization and surface mounting technology.[1] In order to reduce the production cost for MLCCs, the development of inexpensive electrode materials such as base metals (Ni and Cu) is thus actually required.[2,3] However, the base-metal-electroded (BME) capacitors need to be fired under a reducing atmosphere, since the Cu (or Ni) metal is subjective to oxidation during sintering in air. Many approaches, which successfully maintain the excellent dielectric properties of the $BaTiO_3$ materials after sintering in a reducing atmosphere, have been reported.[3–10]

In X7R-type MLCC materials, the capacitance variation ($\Delta C/C$-value) must be within 15% in the temperature regime from -55 to 125 °C. In order to establish the temperature stability of dielectric constant, certain dopant oxides are mixed with $BaTiO_3$ and introduced into the lattice with concentration gradients within each grain. The key factor resulting in a low temperature coefficient of dielectric properties is presumed to be the presence of the core-shell microstructure,[11–14] which can be achieved by critically controlling the doping species and concentration.[15,16] Previously, we reported the effects of Y_2O_3 and MgO additives on the dielectric properties of $BaTiO_3$ materials.[17] In addition to the conventional route for forming core-shell-structured materials, we adopted a simpler approach for preparing low $-\Delta C/C$ capacitor materials, in which the two $BaTiO_3$ constituents possessing different dielectric constant (*K*)–temperature (*T*) characteristics were mixed and sintered to form duplex-structured materials.[18] The dielectric properties, particularly the temperature coefficient of capacitance (TCC), of the $BaTiO_3$ materials were improved markedly but the detailed mechanism is still not well understood.

In this study, we examined the microstructures of these materials in detail using transmission electron microscopy

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(TEM) so as to explore the formation mechanism of the duplex microstructures. We also correlated the materials' microstructures with their dielectric properties, based on these observations.

2. Experimental

In the synthesis of duplex-structured materials, two starting constituents of different dopant content were first prepared. In addition to the commercial $BaTiO_3$ powders (Ba/Ti = 0.998, 0.2 μm size), MnO_2 dopant (0.4 mol%) and $(Ba_{0.6}Ca_{0.4})SiO_3$ sintering aid (3 mol%), where the $(Ba_{0.6}Ca_{0.4})SiO_3$ was prepared by calcining the mixture of $BaCO_3$, $CaCO_3$ and SiO_2, in the proper proportion, at 1100 °C for 2 h, the lightly doped constituent contains only 1.5 mol% Y_2O_3, whereas the heavily doped constituent contains 1.5 mol% Y_2O_3 and 5 mol% MgO, which were designated as "A" and "B" materials, respectively. The duplex-structured $BaTiO_3$ materials were obtained by mixing the lightly doped materials (A) and heavily doped materials (B) of 1:1 molar ratio, which were designated as "A + B" materials. The mixtures were pelletized and then sintered at 1250 °C for 3 h in 10^{-10} Torr P_{O_2} atmosphere, followed by re-oxidation at 1000 °C for 2 h in 80 ppm P_{O_2} atmosphere.

The Cu-paste was screen-printed onto the sintered samples, followed by firing at 900 °C for 10 min in 30 ppm P_{O_2} to serve as electrodes. The dielectric properties of the capacitor materials were measured from −55 to 150 °C using the H.P. 4278 capacitance meter. The crystallographic structure of the as-sintered samples was examined using a Rigaku DMAX-IIB X-ray diffractometer (XRD), and refined further by the Rietveld analysis method (program: GSAS).[19] TEM (Jeol 2000 FXII) with energy dispersive X-ray spectroscope (EDS) system was employed for examining the detailed microstructures and detecting the dopant distribution of the samples.

3. Results and discussion

X7R-type capacitor materials by mixing two components with predesigned *K*–*T* characteristics have been demonstrated in a previous study.[18] Fig. 1a shows typical *K*–*T* characteristics of the $BaTiO_3$ materials thus prepared. The lightly doped $BaTiO_3$ materials possess a large Curie peak (designated as "A", open diamonds, Fig. 1a), whereas the heavily doped $BaTiO_3$ materials show a flat *K*–*T* curve (designated as "B", open squares, Fig. 1a). Both of the constituents possess too large a $\Delta C/C$-value and do not meet the X7R specification (Fig. 1b). However, a significant modification on the *K*–*T* behavior of the materials can be achieved via mixing of the two constituents with A:B in a 1:1 ratio. The Curie peak for the lightly doped $BaTiO_3$ materials at around 120 °C was markedly suppressed and a flat *K*–*T* curve with $\Delta C/C$-value lying within the X7R specification was obtained (designated as "A + B", closed circles, Fig. 1b).

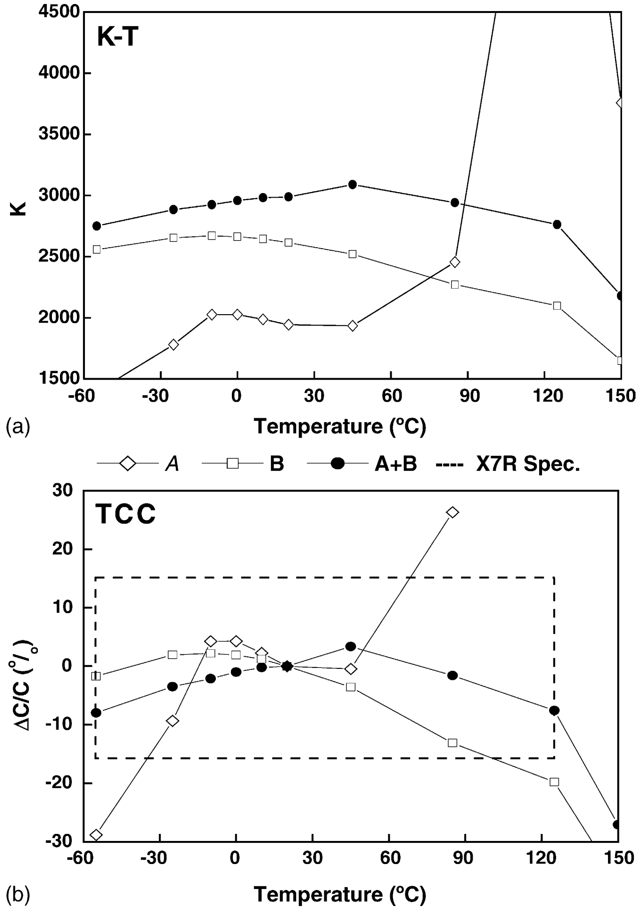

Fig. 1. (a) *K*–*T* properties and (b) capacitance variation, $\Delta C/C$, for duplex-structured $BaTiO_3$ materials, where "A" is the lightly doped constituent, containing 1.5 mol% Y_2O_3 + 0 mol% MgO, "B" is the heavily doped constituent, containing 1.5 mol% Y_2O_3 + 5 mol% MgO, and "A + B" is the duplex-structured materials contain A and B constituents of 1:1 molar ratio.

Room temperature X-ray diffraction profiles of these above $BaTiO_3$ materials are shown in Fig. 2, which reveals that all of the as-sintered samples are of the perovskite-type structure and no additional diffraction peak is observed, implying that all the dopants have entered the $BaTiO_3$ lattice and formed a solid solution. The result agree with that single $BaTiO_3$ solid solution could be obtained without other phases were precipitated in a wide range of $0 \leq x \leq 0.6$ for $(Ba_{1-x}La_x)(Ti_{1-x/2}Mg_{x/2})O_3$ ceramics.[20] In addition, it should be noted that the peak profile for the heavily doped $BaTiO_3$ materials (designated as "A", Fig. 2) are broader in comparison with those of the lightly doped $BaTiO_3$ materials (designated as "B", Fig. 2), while the duplex-structured $BaTiO_3$ materials (designated as "A + B", Fig. 2) possess a middle peak broadening between those of the two end-point constituents. The results indicate that the peak broadening resulted largely from the difference in MgO content, i.e., the MgO additions lead to the formation of multiphase of perovskite structures and thus makes the peak profile broadening. To determine further the amounts of different phases as well as their lattice parameters, the X-ray diffraction pro-

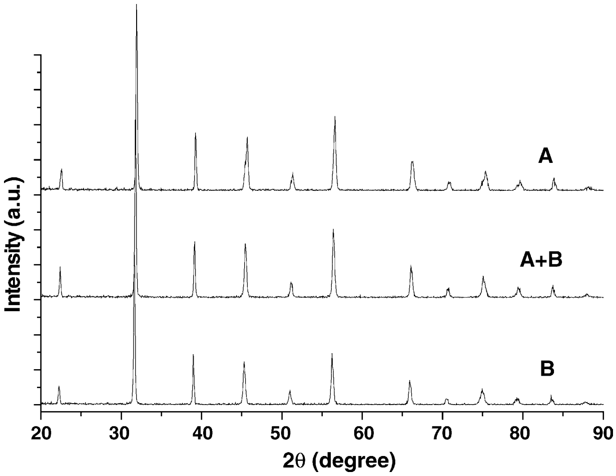

Fig. 2. X-ray diffraction patterns for duplex-structured $BaTiO_3$ materials, where “A” is the lightly doped constituent, containing 1.5 mol% Y_2O_3 + 0 mol% MgO, “B” is the heavily doped constituent, containing 1.5 mol% Y_2O_3 + 5 mol% MgO, and “A + B” is the duplex-structured materials contain A and B constituents of 1:1 molar ratio.

files of the samples were analyzed by the multiphase Rietveld method. Table 1 shows the results of structure refinement, and which indicates that there are two crystalline phases, tetragonal and cubic structures, co-existing in the $BaTiO_3$ samples. Apparently, the volume fraction of cubic-structured $BaTiO_3$ and the lattice parameters of both cubic and tetragonal phases for the heavily doped $BaTiO_3$ materials are larger than that of lightly doped $BaTiO_3$ materials, as well as the tetragonality (*c*/*a* ratio) is inversely proportional to the amount of MgO. The fact that heavily doped $BaTiO_3$ materials (5 mol% MgO) possessed larger lattice constants than that of lightly doped $BaTiO_3$ materials (0 mol% MgO) resulted from the ionic radii of Mg^{2+} in six coordinate is 0.720×10^{-10} m, which is slightly larger to that of Ti^{4+} in six coordinate (0.605×10^{-10} m) since the Mg^{2+} is expected to dissolve in the B site based on the ionic radius.[14,20] From these results, it seems that Mg species play an important role in the modification of crystalline structure in the X7R-type $BaTiO_3$ capacitor materials. This will be further verified by TEM images of these same samples.

Table 1
Crystal structure parameters[a] for the lightly doped constituent, only containing 1.5 mol% Y_2O_3 (designated as “A”), and heavily doped constituent, containing 1.5 mol% Y_2O_3 + 5 mol% MgO (designated as “B”), as well as duplex-structured materials contain lightly doped and heavily doped constituents of 1:1 molar ratio (designated as “A + B”)

Samples	Tetragonal	Cubic	*a*	*c*	Tetragonality (*c*/*a*)
A	0.90		3.9885	4.0252	1.0092
		0.10	3.9930		
B	0.21		4.0023	4.0380	1.0089
		0.79	4.0122		
A + B	0.46		3.9956	4.0317	1.0090
		0.54	4.0015		

[a] The amount of crystal phase in volume fraction, and lattice parameters in angstrom.

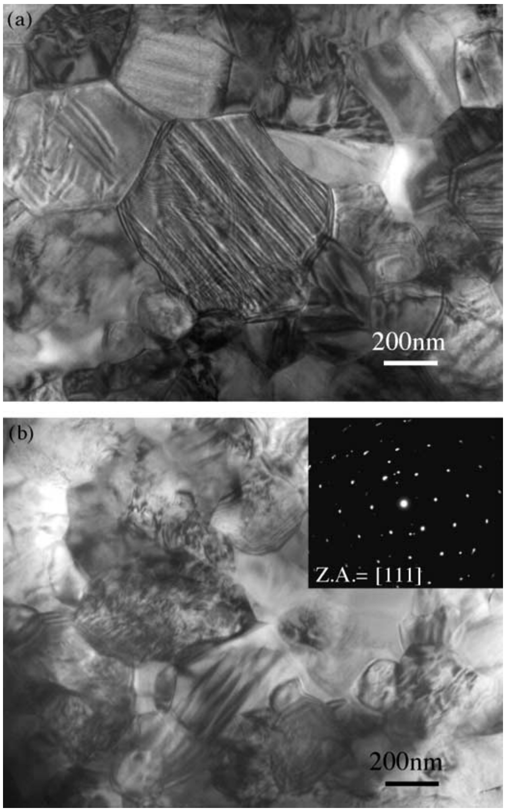

Fig. 3. TEM images of: (a) lightly doped $BaTiO_3$ materials containing only 1.5 mol% Y_2O_3 and (b) heavily doped $BaTiO_3$ materials containing 1.5 mol% Y_2O_3 + 5 mol% MgO. The inset shows the distortion of fundamental spots of a [1 1 1]-zone selected area diffraction pattern for the fine cubic grains in the heavily doped materials.

Fig. 3a shows that the grains of lightly doped materials are larger in size (∼0.5–0.8 μm) and of faceted geometry with sharp grain boundaries. There are no core-shell-structured grains observed. All the grains contain a complex domain structure, indicating that these materials are ferroelectric in nature. In contrast, Fig. 3b reveals that the grains in the heavily doped materials are small (≤0.3 μm), very close to that of the starting powder. It seems that the grain growth in the heavily doped $BaTiO_3$ materials was fully inhibited. According to XRD and TEM analysis, it can be presumed the solute drag effect should be mainly pinning mechanism since no secondary phase and grain boundary pores are present in the heavily doped $BaTiO_3$ materials, and which implies the doped solutes had a very rigorous interaction with the grain boundary and pinned the mobility of the boundary. Moreover, no electrical domain is observable, implying that these grains are paraelectric. Additionally, selected area electron diffraction patterns indicated that most of the grains in the heavily doped materials are of cubic structure, and are highly strained which can be known via observing the distortion of fundamental spots of [1 1 1]-zoned diffraction pattern, shown as the inset in Fig. 3b.

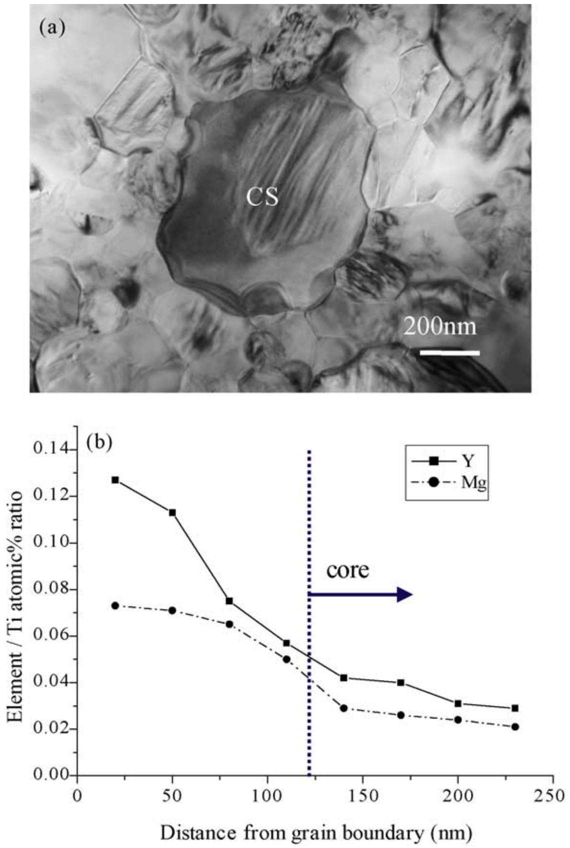

Fig. 4. (a) TEM image of duplex-structured $BaTiO_3$ materials containing lightly doped materials (constituent A) and heavily doped materials (constituent B) of 1:1 molar ratio and (b) distributions of MgO and Y_2O_3 additives in the core-shell structured grain (designated as "CS" (a) for duplex-structured $BaTiO_3$ materials.

Distinct features of microstructure were observed when the mixture of the two constituents was sintered. Fig. 4a shows that small grains (≤0.25 μm) are of single phase with cubic structure and are highly strained, whereas large grains (0.5 μm) always exhibit a core-shell microstructure (designated as "CS", Fig. 4a). No grain with a tetragonal structure similar to that of lightly doped materials is observable. The small cubic grains are probably the originally heavily doped constituent whereas the large grains possibly originate from the lightly doped constituent. As the grains of lightly doped $BaTiO_3$ materials grew, the enlarged region was converted into paraelectric due to the incorporation of large proportion of MgO species, while the originally lightly doped region remains ferroelectric, resulting in a core-shell structure with larger grain size. Fig. 4b shows the distribution of MgO and Y_2O_3 additives in the grain CS (shown in Fig. 4a) as determined by TEM–EDS. It illustrates that MgO and Y_2O_3 species heavily dissolve in $BaTiO_3$ in the shell, and distribute with gradient concentration from the grain boundary to the shell region. The core phase is almost composed of pure tetragonal $BaTiO_3$. It also indicated that temperature-stable dielectric characteristic for the duplex-structured samples is due to the combination of the responses of the cubic-structured and core-shell-structured grains, i.e., mixing the large grains of the core-shell structure with the paraelectric fine grains of the heavily doped constituent, the composition further averages out the capacitance of each constituent, leading to extremely small capacitance variation ($\Delta C/C$) for the $BaTiO_3$ materials. Therefore, the *K*–*T* characteristics of the duplex-structured materials are relatively insensitive to the ratio of the two end-point constituents.

4. Conclusion

X7R-type capacitor materials can be obtained by the duplex-structured process. TEM investigations indicate that the heavily doped constituents of the samples remained as fine grains with paraelectric phase, whereas the lightly doped constituents of the materials grew, resulting in a core-shell microstructure via the incorporation of the MgO species when the mixture of the two constituents was sintered. The unique *K*–*T* characteristics of the samples are ascribed to the duplex structure of the samples, which contain fine grains of cubic structure and large grains of core-shell structure, and hence the capacitance variation ($\Delta C/C$) of the duplex-structured materials is small and insensitive to temperature variation.

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References

1. Sakabe, Y., Takagi, T. and Wakino, K., Dielectric materials for base-metal multilayer ceramic capacitors. *J. Am. Ceram. Soc.*, 1986, **69**, 103–111.
2. Sato, S., Nakano, Y. and Sato, A., Effect of Y-doping on resistance degradation of multilayer ceramic capacitors with Ni electrodes under the highly accelerated life test. *Jpn. J. Appl. Phys.*, 1996, **9B**, 6016–6020.
3. Shizuno, H., Kusumi, S. and Saito, H., Properties of Y5V multilayer ceramic capacitors with Ni electrodes. *Jpn. J. Appl. Phys.*, 1993, **9B**, 4380–4383.
4. Peng, C. J. and Lu, H. Y., Compensation effect in semiconducting barium titanate. *J. Am. Ceram. Soc.*, 1988, **71**, C44–C46.
5. Drodenik, M., Oxygen partial pressure and grain growth in donor-doped $BaTiO_3$. *J. Am. Ceram. Soc.*, 1987, **70**, 311–314.
6. Chan, H. M., Harmer, M. P. and Smyth, D. M., Compensating defects in highly donor-doped $BaTiO_3$. *J. Am. Ceram. Soc.*, 1986, **69**, 507–510.
7. Kahn, M., Influence of grain growth on dielectric properties of Nb-doped $BaTiO_3$. *J. Am. Ceram. Soc.*, 1971, **54**, 455–457.
8. Sumita, S., Ikeda, M., Nakano, Y., Nishiyama, K. and Nomura, T., Degradation of multilayer ceramic capacitors with nickel electrodes. *J. Am. Ceram. Soc.*, 1991, **74**, 2739–2746.
9. Burn, I., Ceramic disk capacitor with base-metal electrode. *Am. Ceram. Soc. Bull.*, 1978, **57**, 600–604.

10. Yang, W. C., Hu, C. T. and Lin, I. N., Effect of Y_2O_3 doping on the electrical properties of base-metal-electroded capacitor materials. *Ferroelectrics*, 2002, **270**, 1321–1326.
11. Molokhia, N. M., Issa, M. A. A. and Nasser, S. A., Dielectric and X-ray diffraction studies of barium titanate doped with yttrium. *J. Am. Ceram. Soc.*, 1984, **67**, 289–291.
12. Park, Y. and Kim, H. G., Dielectric temperature characteristics of cerium-modified barium titanate ceramics with core-shell grain structure. *J. Am. Ceram. Soc.*, 1997, **80**, 106–112.
13. Hennings, D. and Rosenstein, G., Temperature-stable dielectrics based on chemically inhomogeneous $BaTiO_3$. *J. Am. Ceram. Soc.*, 1984, **67**, 249–254.
14. Kishi, H., Mizuno, Y. and Chazono, H., Base-metal-electrode multilayer ceramic capacitors: past, present and future perspectives. *Jpn. J. Appl. Phys.*, 2003, **42**, 1–15.
15. Saito, H., Chazono, H., Kishi, H. and Yamaoka, N., X7R multilayer ceramic capacitors with nickel electrodes. *Jpn. J. Appl. Phys.*, 1991, **9B**, 2307–2310.
16. Mizuno, Y., Okino, Y., Kohzu, N., Chazono, H. and Kishi, H., Influence of microstructure evolution on electrical properties of multilayer capacitor with Ni electrodes. *Jpn. J. Appl. Phys.*, 1998, **9B**, 5227–5231.
17. Yang, W. C., Hu, C. T. and Lin, I. N., Effect of Y_2O_3/MgO co-doping on the electrical properties of base-metal-electroded $BaTiO_3$ materials. *J. Eur. Ceram. Soc.*, 2004, **24**, 1479–1483.
18. Yang, W. C., Hu, C. T. and Lin, I. N., Base-metal-electroded $BaTiO_3$ capacitor materials with duplex microstructures. *J. Am. Ceram. Soc.*, 2004, **87**, 851–858.
19. Larson, A. C. and Von Dreele, R. B., *General structure analysis system*, Lansce, MS-H805, Los Alamos National Laboratory, 1985.
20. Watanabe, K., Ohsato, H., Kishi, H., Okino, Y., Kohzu, N., Iguchi, Y. *et al.*, Solubility of La–Mg and La–Al in $BaTiO_3$. *Solid State Ionics*, 1998, **108**, 129–135.