

# High-Temperature Capacitor Materials Based on Modified BaTiO<sub>3</sub>

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High-temperature capacitor materials sintered at 1120°C were prepared in a BaTiO<sub>3</sub> (BT)-Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub> (NBT)-Nb<sub>2</sub>O<sub>5</sub>-ZnO-CaZrO<sub>3</sub> system. The Curie temperature of BaTiO<sub>3</sub> was increased by NBT doping, and a secondary phase occurred when adding ≥5 mol% NBT. The effects of Nb<sub>2</sub>O<sub>5</sub>, ZnO, and CaZrO<sub>3</sub> on the dielectric properties and the microstructure of BT ceramics doped with 1 mol% NBT were analyzed. The overall dielectric constant decreased when the Nb<sub>2</sub>O<sub>5</sub> content increased, and increased when the ZnO content increased. The dielectric constant peak at the Curie temperature was effectively depressed, and a broad secondary dielectric constant peak appeared at 60°C when the ZnO concentration was ≥4.5 mol%. Significant grain growth was observed by scanning electron microscope (SEM) analysis as the amount of ZnO increased. The high-temperature capacitor specification (−55°C to +175°C, ΔC/C<sub>25°C</sub> less than ±15%) is met when 7 mol% to 8 mol% CaZrO<sub>3</sub> is added.

**Key words:** Barium titanate, high-temperature capacitor, sodium bismuth titanate, electrical properties

## INTRODUCTION

Since the discovery of the high dielectric properties of BaTiO<sub>3</sub> (BT) ceramics, many modifications to this compound have been made in order to achieve temperature-stable capacitors with satisfactory operational capacity. BT has a tetragonal structure at room temperature and it changes into a cubic structure at the Curie temperature ( $T_C$ ). Therefore, pure BT has a strong temperature dependence of the dielectric constant due to its sharp phase transition at  $T_C$ . Many dopants have been added to pure BT to achieve temperature-stable dielectric properties. Some multilayer ceramic capacitors (MLCCs), exhibiting temperature-stable dielectric properties (ΔC/C<sub>25°C</sub> less than ±15%) over the temperature range from −55°C to 125°C (X7R characteristic of the EIA standard) or −55°C to 150°C (X8R characteristic of the EIA standard), have been developed in

such systems as BT-Nb<sub>2</sub>O<sub>5</sub>-Co<sub>2</sub>O<sub>3</sub>,<sup>1,2</sup> BT-MgO-Re<sub>2</sub>O<sub>3</sub> (Re = rare earth),<sup>3–6</sup> and BT-Nb<sub>2</sub>O<sub>5</sub>-ZnO.<sup>7</sup>

In recent years, MLCCs have been applied to automobile parts, such as the engine electronic control unit, antilock brake system, and programmed fuel injection. Some of these modules are subject to high temperatures above 150°C when working in an engine space, and conventional dielectric ceramic compositions cannot be employed. Thus there are great needs to develop high-temperature MLCCs. However, little research has been done on this subject, because it is difficult for BT to meet the requirement of ΔC/C<sub>25°C</sub> of less than ±15% at high temperatures due to the rapid drop of capacitance above  $T_C$  according to the Curie–Weiss law.<sup>8</sup> Therefore, increasing the Curie temperature of BT is suitable for high-temperature capacitance stability of MLCCs. Rare-earth elements with a smaller ionic radius, such as Tm, Yb, Lu, Sc, and Y, were found to be effective in increasing the  $T_C$  of BT ceramics.<sup>3,5</sup> When a core-shell structure is formed in BaTiO<sub>3</sub>-MgO-Re<sub>2</sub>O<sub>3</sub> (Re = Tm, Yb, Lu, and Er) systems, a mismatch between grain core and grain

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shell causes substantial internal stress, and shifts the  $T_C$  to higher temperatures.

Kobayashi et al.<sup>9</sup> have studied the temperature dependence of capacitance change ( $\Delta C/C$  versus  $T$ , where  $\Delta C/C = (C - C_{25^\circ\text{C}})/C_{25^\circ\text{C}}$ , and  $C$  and  $C_{25^\circ\text{C}}$  represent the capacitance value at the measuring temperature and at 25°C, respectively) of BT-based MLCCs and have suggested that the high-temperature peak value of the  $\Delta C/C$  versus  $T$  curve will decrease as dielectric layers become thinner. Therefore, these materials are not suitable for MLCCs applications even though they fit the characteristic of  $\Delta C/C_{25^\circ\text{C}}$  of less than  $\pm 15\%$  in thick disc form. So increasing the high-temperature peak value of the  $\Delta C/C$  versus  $T$  curve became another key approach for the development of high-temperature MLCCs.

Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub> (NBT) is an attractive lead-free piezoelectric material because of its strong ferroelectricity at room temperature and high Curie temperature of 320°C.<sup>10</sup> In addition, NBT can form solid solutions with BT because it shares the same perovskite structure.<sup>11,12</sup> In our previous report,<sup>13</sup> the Curie temperature of BT was greatly increased by adding 1 mol% NBT, and MLCCs satisfying the X8R characteristic of the EIA standard were developed by adding BiNbO<sub>4</sub> to a BT-NBT composite. In this study, high-temperature MLCCs meeting the specification ( $-55^\circ\text{C}$  to  $+175^\circ\text{C}$ ,  $\Delta C/C_{25^\circ\text{C}}$  less than  $\pm 15\%$ ) were developed in a BT-NBT-Nb<sub>2</sub>O<sub>5</sub>-ZnO system.

## EXPERIMENTAL PROCEDURE

NBT powder was synthesized using the conventional solid-state method from reagent-grade Bi<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and Na<sub>2</sub>CO<sub>3</sub> powders. The starting materials were mixed and ball-milled in ethyl alcohol for 12 h with stabilized zirconia balls. Then the mixture was dried and calcined at 800°C for 2 h. Powders of hydrothermal BT (BT-04, Guoteng, China) and 1 mol% NBT were mixed in deionized water by ball-milling and then calcined at 1150°C for 2 h. The powder obtained is denoted BTNBT-0. The Curie temperature of BaTiO<sub>3</sub> can be effectively increased by calcining BT with NBT in advance, which will be discussed later. Samples were prepared using the conventional ceramic processing technique with powders of BTNBT-0, 0.5 mol% to 2.0 mol% Nb<sub>2</sub>O<sub>5</sub>, 0.5 mol% to 6.0 mol% ZnO, and 5.0 mol% to 8.0 mol% CaZrO<sub>3</sub>. The mixed powders were ball-milled in deionized water for 8 h. The prepared ceramic powders were pressed into disk form ( $\sim 10$  mm diameter,  $\sim 1$  mm thick) by mixing ceramic powders with 3 wt.% polyvinyl alcohol (PVA) binder. After debinding, the disks were finally fired at 1120°C for 2 h in air.

Ag was applied on both sides of the as-fired samples after firing to obtain contact electrodes. Dielectric measurements of the samples were performed using an LCR meter (YY2812), autocontrolled by

computer, at 1 kHz and 1.0 V root-mean-square (rms) in the temperature range from  $-55^\circ\text{C}$  to  $175^\circ\text{C}$ . Microstructures of the ceramics were observed with an S-530 scanning electron microscope (SEM). X-ray diffraction (XRD) analysis was carried out using a Philips X'Pert diffractometer over the range of  $2\theta = 20$  deg to 80 deg with CuK <sub>$\alpha$</sub>  radiation.

## RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the dielectric constants of BT ceramics sintered at 1120°C for 2 h with additions of 0.1 mol% to 10 mol% NBT. The Curie temperature of BT ceramics increased as the amount of NBT increased, due to the substitution of Bi<sup>3+</sup> with Ba<sup>2+</sup> ions and the high Curie temperature of NBT ( $T_C = 320^\circ\text{C}$ ). When 0.1 mol% to 10 mol% NBT was added, the Curie temperature was remarkably increased to 129°C, 140°C, 145°C, and 173°C, respectively. In our previous study, the Curie temperature of BaTiO<sub>3</sub> moved to 128°C when 10 wt.% NBT was added together with other additives.<sup>14</sup> Therefore, it

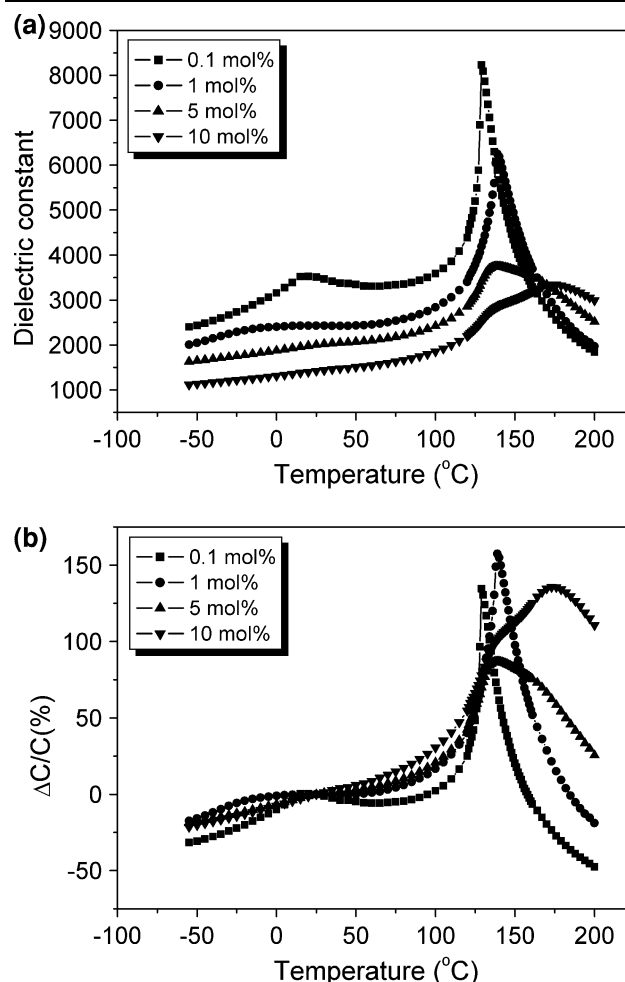


Fig. 1. Temperature dependence of (a) dielectric constant and (b)  $\Delta C/C$  of BaTiO<sub>3</sub> ceramics doped with 0.1 mol% to 10 mol% NBT.

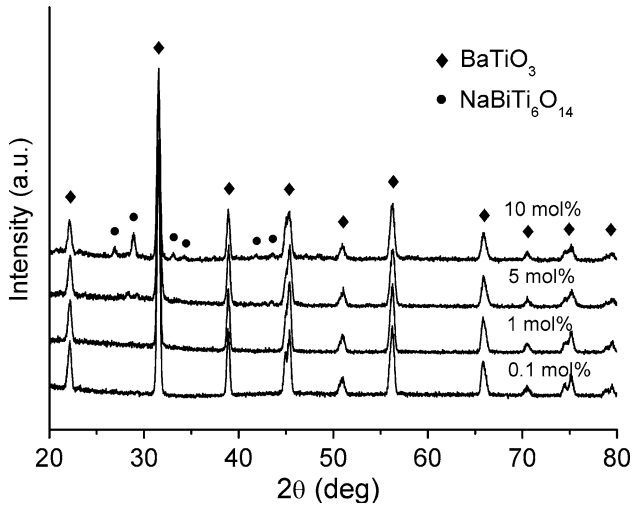


Fig. 2. XRD patterns for BaTiO<sub>3</sub> ceramic doped with various amounts of NBT.

is more effective to enhance the Curie temperature of BaTiO<sub>3</sub> by precalcining BT with NBT. It was also observed that the dielectric constant decreased over a wide temperature range with increasing NBT content. Moreover, the dielectric constant peak at  $T_C$  was markedly suppressed and broadened. This possibly resulted from a diffuse phase transition caused by an inhomogeneous distribution of Bi<sup>3+</sup>, Na<sup>+</sup>, and Ba<sup>2+</sup> in local areas when NBT and BT formed solid solutions. Figure 1b shows that the capacitance change ( $\Delta C/C$ ) at high temperature is enhanced by adding NBT. This change is helpful for us to improve the high-temperature stability of BT ceramics because the dielectric constant of pure BT decreases sharply above  $T_C$ .

XRD patterns of NBT-doped BT ceramics are shown in Fig. 2. It is obvious that, when the addition of NBT was lower than 1 mol%, a single perovskite BaTiO<sub>3</sub> phase was formed after sintering at 1120°C for 2 h. In the case of 5 mol% NBT addition, some extra peaks suggested the existence of a secondary phase, and the amount of the secondary phase grains increased with 10 mol% NBT doping. The secondary phase was identified as NaBiTi<sub>6</sub>O<sub>14</sub>.

Figure 3 shows the temperature dependence of the dielectric constants of this ceramic system with various Nb<sub>2</sub>O<sub>5</sub> and ZnO contents, respectively. As shown in Fig. 3a, two dielectric constant peaks were observed at 142°C and 35°C, respectively, in the sample doped with 0.5 mol% Nb<sub>2</sub>O<sub>5</sub>, which was very likely due to the formation of a core-shell structure in this system. Park et al.<sup>15</sup> have suggested that the dielectric constant peaks at the Curie temperature and lower temperature are correlated with the ferroelectric–paraelectric phase transition of grain core and grain shell, respectively, for core-shell structure grained ceramics. Therefore, we can surmise that the maximum dielectric constant at 142°C is determined by the ferroelectric–paraelectric

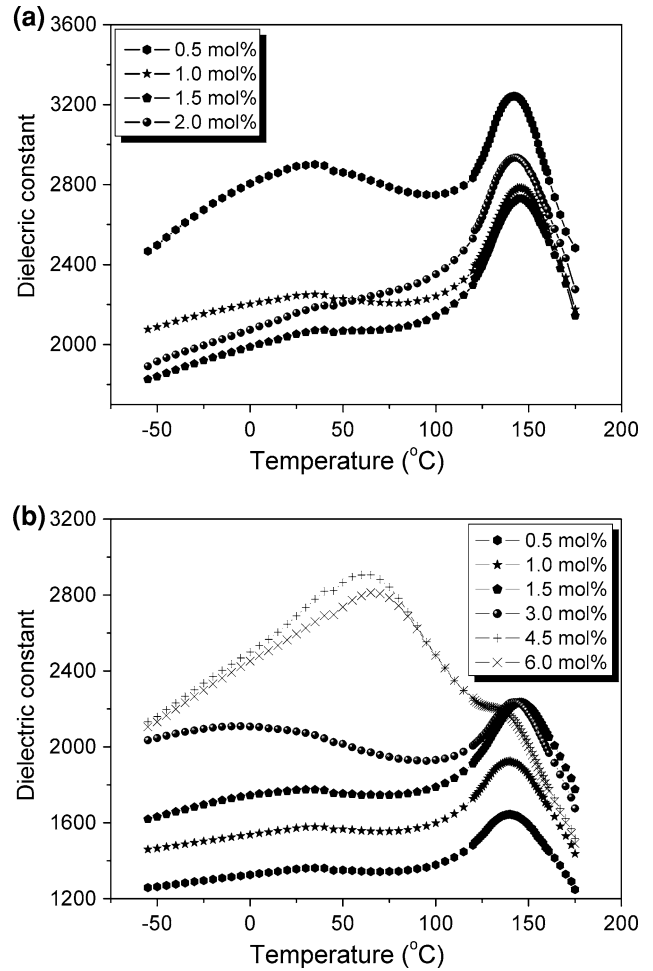


Fig. 3. Temperature dependence of the dielectric constant of the ceramic system as a function of (a) Nb<sub>2</sub>O<sub>5</sub> and (b) ZnO content.

phase transition of the unreacted pure BaTiO<sub>3</sub> grain core, whereas the broad secondary peak appearing at a lower temperature of 35°C is associated with the phase transition of the heavily doped grain shell. The overall dielectric constant decreased with increasing Nb<sub>2</sub>O<sub>5</sub> content. The broad peak near 35°C became increasingly ambiguous as the amount of Nb<sub>2</sub>O<sub>5</sub> increased, and finally disappeared when 2 mol% Nb<sub>2</sub>O<sub>5</sub> was added.

Figure 3b shows that the overall dielectric constant is enhanced gradually with increasing ZnO concentration. This is attributed to the increase of density and grain size, which is gained by increasing the ZnO content because ZnO addition is helpful for sintering. When the ZnO content was lower than 1.5 mol%, the dielectric constant peak at the Curie temperature was dominant. However, as the amount of ZnO was increased further, the broad dielectric constant peak at lower temperature was enhanced. On the contrary, the dielectric constant peak at the Curie temperature was effectively depressed for a ZnO concentration  $\geq 4.5$  mol%, and a broad dielectric constant peak appeared at about 60°C. We speculate that a core-shell structure is

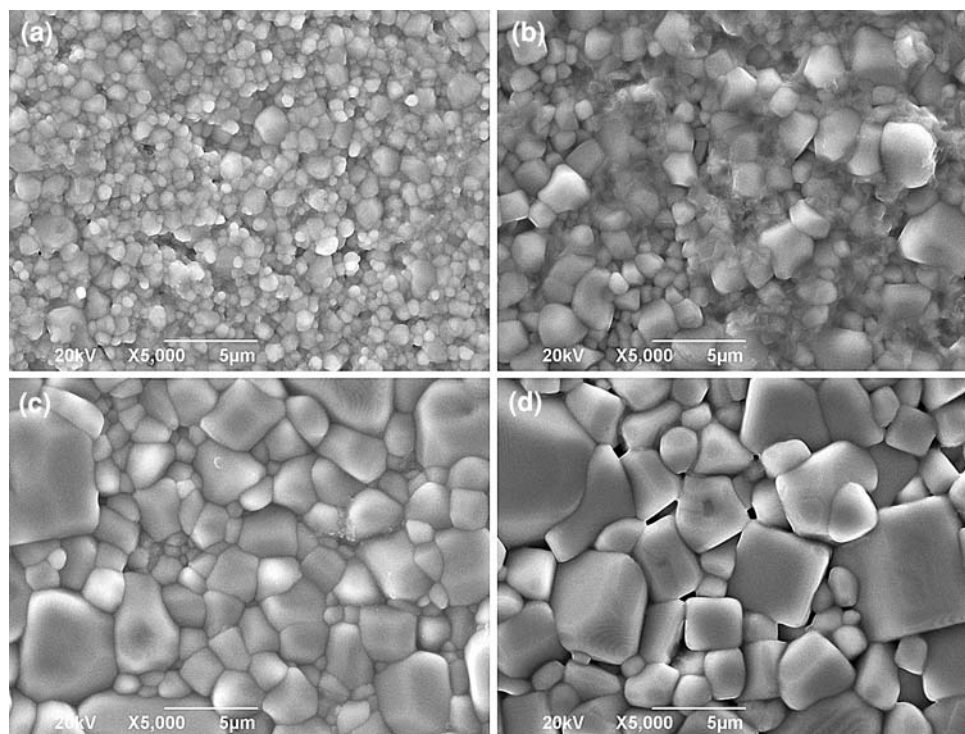


Fig. 4. SEM micrographs of samples doped with various ZnO contents (a) 0.5 mol% (b) 1.0 mol% (c) 3.0 mol%, and (d) 4.5 mol%.

formed in this system because the low diffusivity of Nb<sup>5+</sup> ions will inhibit Zn<sup>2+</sup> ions from diffusing into the BaTiO<sub>3</sub> lattice. When the ZnO addition is lower than 1.5 mol%, the grain shell was thinner, so the dielectric constant at lower temperature was lower. Swilam and Gadalla<sup>16</sup> found that a secondary liquid phase occurred when the amount of ZnO was higher than 0.7 mol%. Therefore, the liquid produced by ZnO doping during sintering will cause grain growth and promote the diffusion of additive ions into the BaTiO<sub>3</sub> lattice. In the case of 3 mol% ZnO addition, the grain shell became thicker so that the dielectric constant at lower temperature was enhanced. When the amount of ZnO was higher than 4.5 mol%, the core-shell structure was presumed to be almost destroyed, resulting from significant grain growth and overdiffusion of additives. Therefore, a broad dielectric constant peak appeared at 60°C. Additionally, the Curie temperature was also decreased.

SEM micrographs for samples doped with various ZnO contents are shown in Fig. 4. With the addition of 0.5 mol% ZnO, a homogeneous and fine-grained microstructure was observed. As the ZnO concentration increased further, a significant increase in grain size was observed due to the presence of a secondary liquid phase resulting from ZnO doping. In the case of 4.5 mol% ZnO addition, abnormal grain growth occurred, resulting in the collapse of the core-shell structure.

Figure 5 shows the temperature dependence of the dielectric constants and capacitance changes

( $\Delta C/C_{25^\circ\text{C}}$ ) for samples doped with various CaZrO<sub>3</sub> contents sintered at 1120°C for 2 h. The dielectric constant over a wide temperature range from -55°C to 175°C decreased with increasing CaZrO<sub>3</sub> content. Especially, the dielectric constant peak at the Curie temperature was effectively depressed. Therefore, the temperature dielectric constant curves became flatter with increasing CaZrO<sub>3</sub> content. The curves of samples doped with 7 mol% to 8 mol% CaZrO<sub>3</sub> satisfied the high-temperature capacitor specification (-55°C to +175°C,  $\Delta C/C_{25^\circ\text{C}}$  less than  $\pm 15\%$ ), which is surrounded by a rectangle in Fig. 5b. The temperature characteristic (TC) of the dielectric constant was modified due to the formation of (Ba,Ca)(Ti,Zr)O<sub>3</sub> grain shells produced by the reaction between CaZrO<sub>3</sub> and BaTiO<sub>3</sub> during sintering. The volume fraction of grain shell increased, whereas that of grain core decreased, as the amount of CaZrO<sub>3</sub> increased, resulting in flat TC curves for samples doped with 7 mol% to 8 mol% CaZrO<sub>3</sub>.

## CONCLUSION

The Curie temperature of BaTiO<sub>3</sub> ceramics was shifted to higher temperatures as the NBT content was increased. Incorporation of 1 mol% NBT increased the Curie temperature to 140°C. XRD analysis indicated that a secondary phase occurred with  $\geq 5$  mol% NBT doping. The overall dielectric constant of this system ceramics decreased when Nb<sub>2</sub>O<sub>5</sub> and CaZrO<sub>3</sub> contents increased. On the other hand, an increase of ZnO content enhanced the

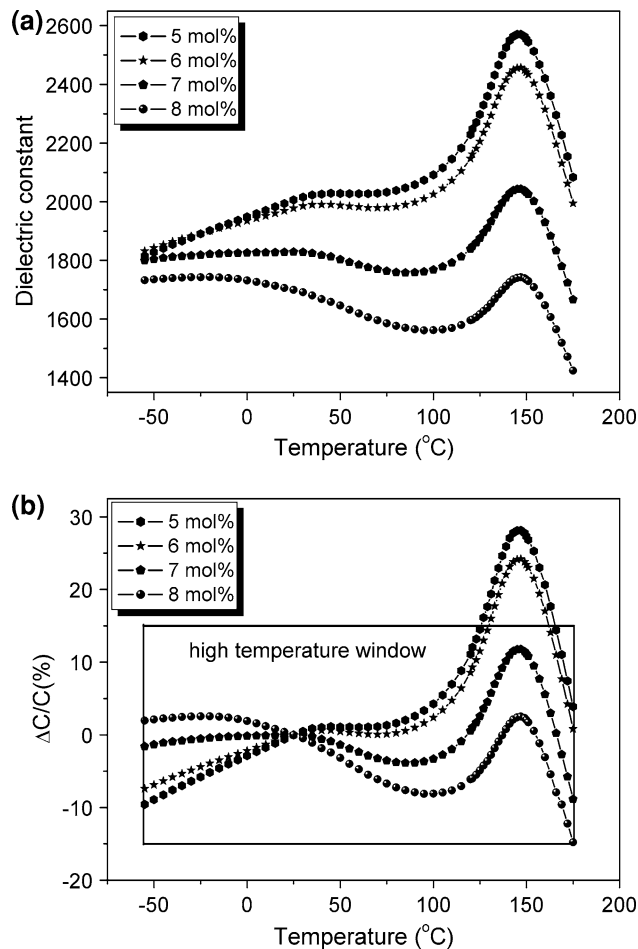


Fig. 5. Temperature dependence of (a) the dielectric constant and (b)  $\Delta C/C$  of samples doped with various  $\text{CaZrO}_3$  contents.

dielectric constant over a wide temperature range from  $-55^\circ\text{C}$  to  $175^\circ\text{C}$ . However, in the case of  $\geq 4.5$  mol% ZnO addition, the dielectric constant peak at  $T_C$  was noticeably depressed, and a broad

secondary dielectric constant peak appeared at  $60^\circ\text{C}$ , indicating the collapse of the core-shell structure. SEM revealed that a fine-grained microstructure was gained by adding 0.5 mol% ZnO and abnormal grain growth happened when the ZnO concentration was  $\geq 4.5$  mol%. The samples doped with 7 mol% to 8 mol%  $\text{CaZrO}_3$  met the high-temperature capacitor specification, with a dielectric constant greater than 1800,  $\Delta C/C_{25^\circ\text{C}}$  ( $-55^\circ\text{C}$  to  $+175^\circ\text{C}$ ) lower than  $\pm 15\%$ , and sintering temperature lowered to  $1120^\circ\text{C}$ .

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