

Dielectric Properties of Zr-doped (Ba,Sr,Ca)TiO₃ Thick Films for Microwave Phase Shifters

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(Ba,Sr,Ca)TiO₃ powders, prepared by the sol-gel method, were mixed with organic binder and the BSCT thick films were fabricated by the screen printing techniques on alumina substrates. All the BSCT thick films, sintered at 1420°C, showed the typical XRD patterns of a perovskite polycrystalline structure. The average grain sizes decreased with increasing amounts of ZrO₂, and the BSCT(40/40/20) thick films doped with 2wt% MnO₂ showed a value of 8μm. The thickness of thick films by four-cycle on printing/drying was approximately 95μm. The relative dielectric constant decreased with increasing Ca content and MnO₂ doping amount. The relative dielectric constant, dielectric loss and tunability of the BSCT(50/40/10) thick films doped with 2.0wt% ZrO₂ were 772, 0.184% and 15.62%, respectively.

Keywords : (Ba,Sr,Ca)TiO₃, Thick film, Screen printing, Dielectric properties, Tunability

1. INTRODUCTION

Perovskite type BaTiO₃ ceramics are the most important electronic materials for use in multilayer ceramic capacitors, positive temperature coefficient (PTC) thermistors and piezoelectric transducers. Ferroelectric BaTiO₃ ceramics have recently attracted great interest as capacitor materials for dynamic random access memories (DRAM) [1] and tunable microwave devices [2]. Tuning of the microwave devices can be achieved by ferroelectric ceramics. The desired characteristics of the dielectric material of choice for phase array applications should be moderate to low dielectric constant at microwave frequencies, low dielectric loss and a large variation of the dielectric constant with applied DC biasing field. Several materials have been proposed for such application. However, the high inherent material loss and high dielectric constant of BaTiO₃ system bulk ceramics have restricted its application in phased array antennas.

Ferroelectric thick film materials possess merits of bulk materials and thin films. Devices made from thick film not only works at low voltage and high frequency,

can be compatible with semiconductor integrated circuits but also possess superior electric properties, approaching close to bulk values.

In this paper, BaTiO₃ powders, partially substituted with Sr⁺² and Ca⁺² ions at the A-sites (Ba⁺² ions) and Zr⁺⁴ ions at the B-sites (Ti⁺⁴ ions), were prepared by the sol-gel method in order to decrease the phase transition temperature to below 0°C and to produce specimens with better dielectric properties for application in microwave phase shifters. (Ba,Sr,Ca)TiO₃ thick films were fabricated by the screen printing method which yields a high productivity and good cost performance. The structural and dielectric properties on the composition ratio and the ZrO₂ content were examined for microwave device applications.

2. EXPERIMENTAL

The chemical compositions of the specimens are given by the formula (Ba_{0.6-x}Sr_{0.4}Ca_x)TiO₃ (BSCT) + y wt% ZrO₂ (x=0.10, 0.15, 0.20, y=0~3.0). These BSCT compositions gave a transition temperature below room

temperature. BSCT powders, started with mixture of Ba acetate, Sr acetate hemihydrate, Ca acetate monohydrate and Ti isopropoxide, were prepared by the sol-gel method. Acetic acid and 2-methoxyethanol were used as solvents. Ba, Sr and Ca acetate were dissolved in acetic acid, and then the solution was heated to 120°C for the evaporation of water. After cooling, Ti isopropoxide, dissolved in 2-methoxyethanol, was added to the solution. The mixed solution was refluxed and then 2-methoxyethanol and water were added to the solution for stabilization and hydrolysis, respectively. The powder precursors were dried and then calcined at 900°C for 2h in a high purity alumina crucible. After dopant of ZrO₂ was added to the calcined powders, these powders were mixed and ground by planetary ball milling.

The screen-printable pastes were prepared by kneading the ground BSCT powder with 30wt% of organic binder (Ferro. B75001) in a non-bubbling kneader (NBK-1, Kyoto Electro.). High purity alumina was used as a substrate. The bottom electrodes were prepared by screen printing Pt paste and firing at 1450°C for 20min. After screen printing the BSCT paste using a 200 mesh screen mask, printed films were allowed to level for 10min and then dried at 80°C for 30min. These processes from printing to drying were repeated four times to obtain a desired thickness. The thick films were sintered at 1420°C for 2h in the closed alumina crucible, with an intermediate 2h isothermal at 600°C to remove the organic components. The upper electrodes were fabricated by screen printing the Ag paste and then firing at 850°C for 30min.

X-ray diffraction (XRD) and scanning electron microscopy (SEM) were introduced in order to analyze the crystallinity and the microstructure of BSCT specimen, respectively. The dielectric properties were measured using on impedance material analyzer (HP 4294). The % tunability was determined using the following equation; % tunability = $\{K(0) - K(V_{\text{appl.}})\} / K(0)$, where $K(0)$ is the relative dielectric constant without DC bias and $K(V_{\text{appl.}})$ is the relative dielectric constant with $V_{\text{appl.}}$. The tunability measurements were taken as a function of applied electric field, with ranged from 0 to 30 kV/cm.

3. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns of the ZrO₂-doped BSCT(40/40/20) thick films sintered at 1420°C. All the BSCT thick films showed the typical XRD patterns of a perovskite polycrystalline structure and no pyrochlore phase was observed. The lattice constant of BSCT specimens decreased with increasing Ca content, because the radius of the Ca²⁺ ion (0.099 nm) is smaller than that of the Ba²⁺ ion (0.135nm). The

values of the BSCT(50/40/10), BSCT(45/40/15), and BSCT(40/40/20) thick films are 0.3932 nm, 0.3928 nm, and 0.3924 nm, respectively.

Figure 2 shows the surface and cross-sectional SEM micrographs of the BSCT(40/40/20) thick films for various ZrO₂ contents. The grain size decreased with increasing ZrO₂ amount because a portion of the doping Zr ions precipitate out of the normal grains and stay at grain boundaries which subsequently resist the grain growth. The BSCT(40/40/20) thick films doped with 2wt% ZrO₂ exhibited a dense and uniform grain structure and the average grain size was about 8μm. The thickness of all the specimens was approximately 95μm.

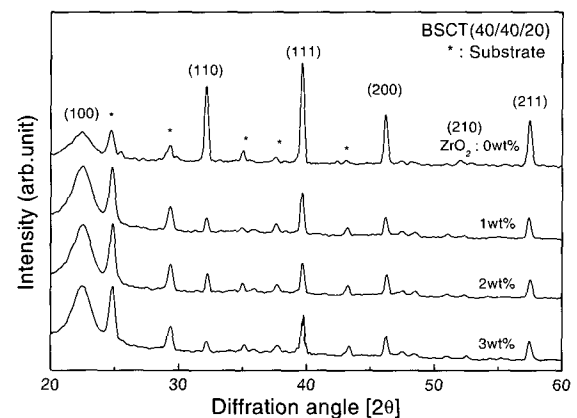


Fig. 1. XRD patterns of the ZrO₂-doped BSCT(40/40/20) thick films.

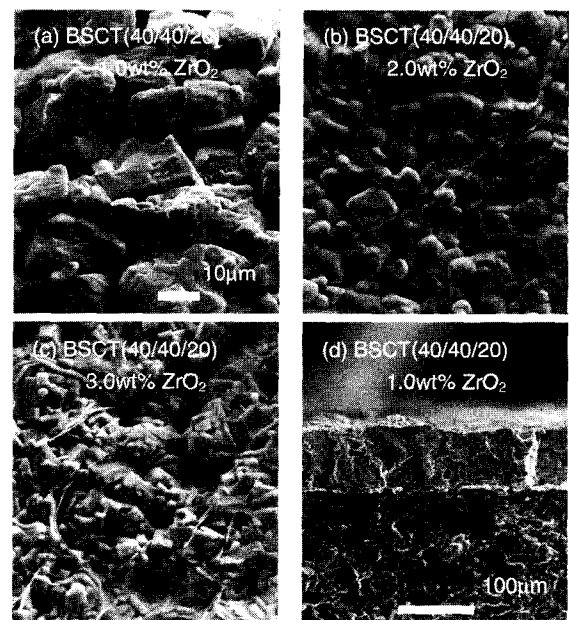


Fig. 2. Surface and cross-sectional SEM micrographs of the BSCT(40/40/20) thick films for various ZrO₂ contents.

Figure 3 shows the variation of relative dielectric constant and dielectric loss of BSCT thick films as a function of temperature for various ZrO₂ contents at 1MHz. The relative dielectric constant of BSCT specimens decreased with increasing ZrO₂ amount due to the effect of the decreasing of grain size and substantial replacement of Ti⁴⁺ ion by the Zr⁴⁺ ion in

perovskite structure [3]. The Curie temperature of BSCT specimens decreased with decreasing Ba/(Sr+Ca) ratio. For substitution Sr²⁺-Ba²⁺, the bonding force between the A-site ion and the oxygen ion of ABO₃ perovskite structure becomes stronger because the radius of the Ba²⁺ ion is larger than that of the Sr²⁺ ion (0.113nm): the bonding force Ti-O(Sr), therefore, becomes weaker than

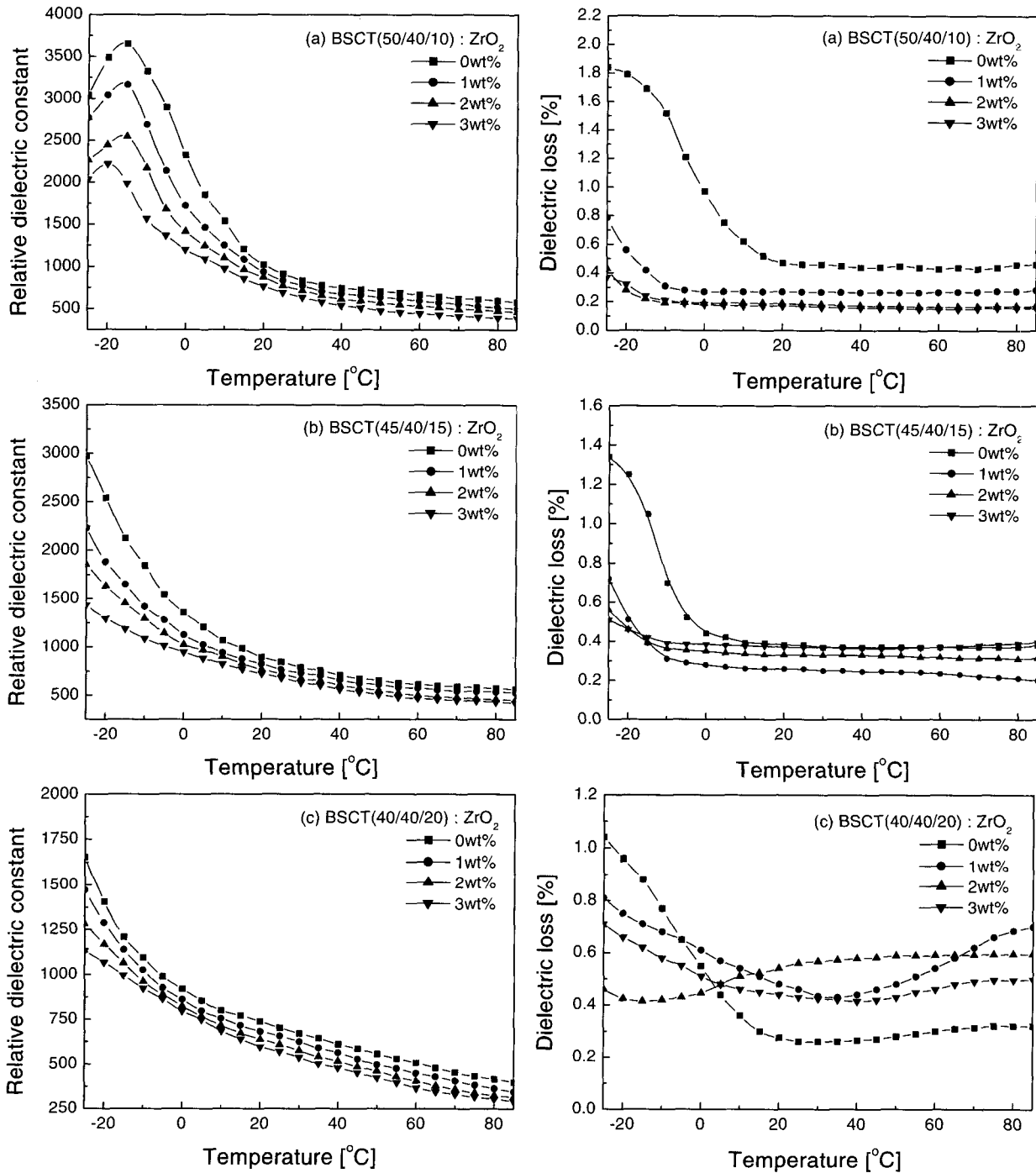


Fig. 3. Relative dielectric constant and dielectric loss as a function of temperature for BSCT thick films with various ZrO₂ contents.

the Ti-O(Ba) bond. The weakening of the Ti-O bond leads to a weaker distortion of the octahedron and brings about a decrease in the *c/a* ratio, thus inducing a drop in the Curie temperature[4]. The dielectric loss of all BSCT specimens was less than 0.006 at room temperature. This small value is enough for applications to tunable microwave devices. The low dielectric loss serves to decrease the insertion loss and, hence, to increase the phase shifting per decibel. The operation frequency of the devices can be extended by reducing the dielectric

loss. The relative dielectric constant and dielectric loss of the BSCT(50/40/10) thick films doped with 2.0wt% ZrO₂ were 772 and 0.184%, respectively.

Figure 4 shows the variation of the relative dielectric constant of BSCT thick films as a function of frequency for various ZrO₂ contents. The relative dielectric constant decreases in the measured frequency range from 0.5GHz to 1GHz and gradually saturates at around 1GHz. This suggests that the relaxation frequency of the dipolar polarization is about 0.7GHz for all specimens.

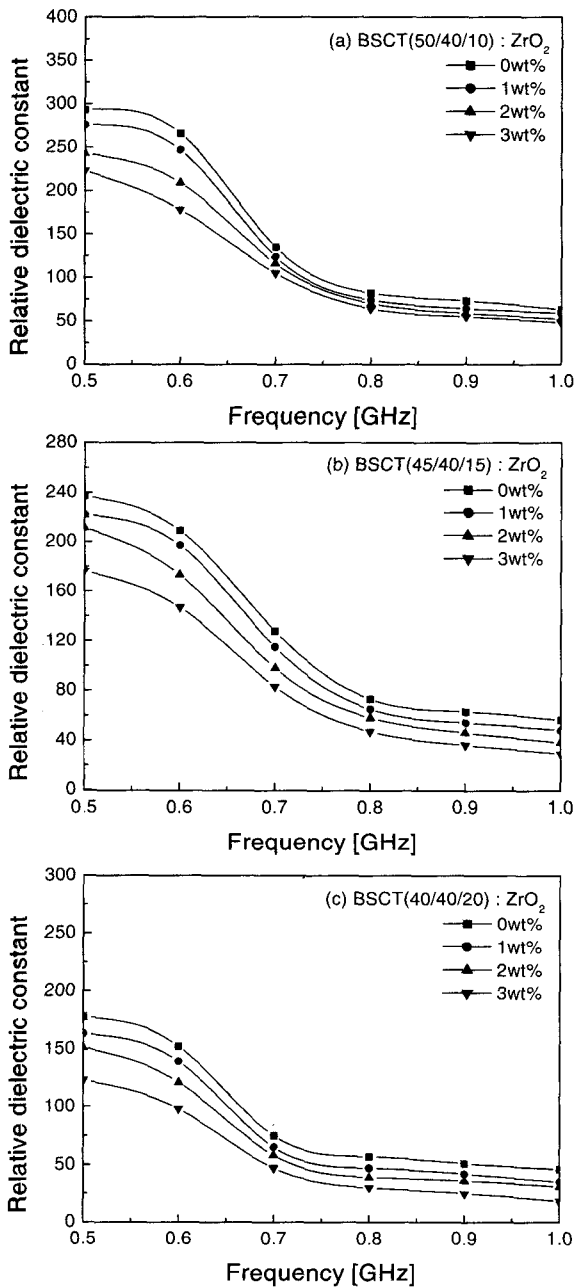


Fig. 4. Relative dielectric constant as a function of frequency for BSCT thick films with various ZrO₂ contents.

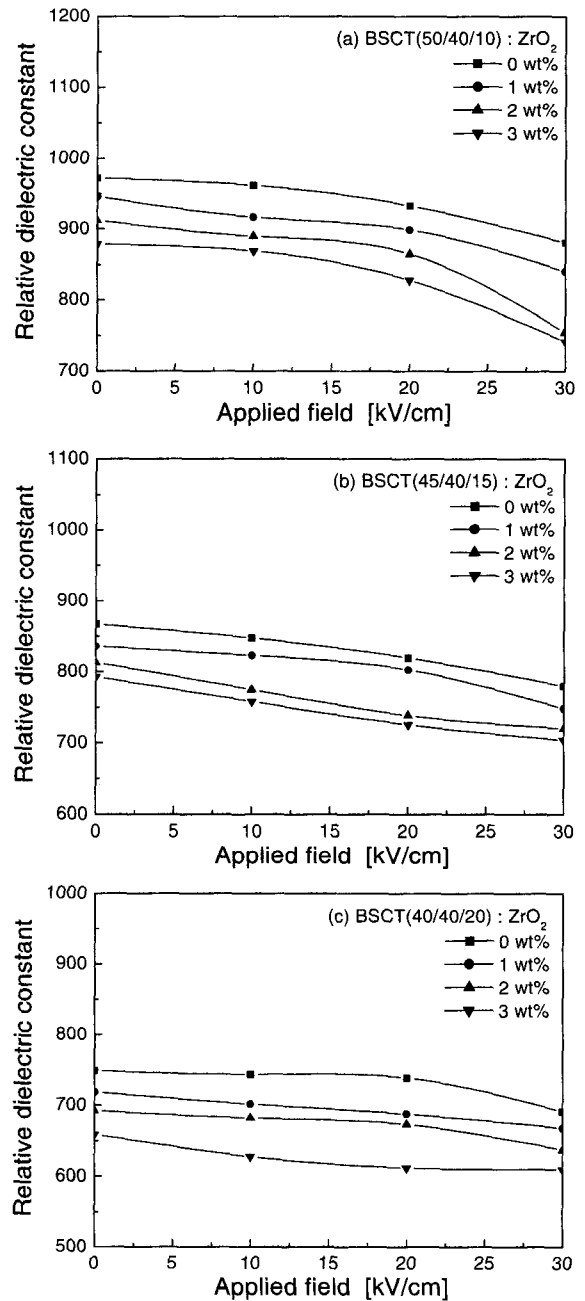


Fig. 5. Relative dielectric constant as a function of the DC electric field for BSCT thick films with various ZrO₂ contents.

Figure 5 shows the applied DC field dependence of the relative dielectric constant for BSCT thick films at 1MHz. The relative dielectric constant of all specimens non-linearly decreased with increasing the applied DC field. This is because the applied electric field acts on the non-ferroelectric grains in such a way as to induce a ferroelectric state in these grains [5]. Also, the non-linear dependence of the dielectric constant on the applied DC electric field results from the chemical inhomogeneities and/or strain between the grains and grain boundaries in polycrystalline specimens [6].

Figure 6 shows the tunability of BSCT thick films as a function of ZrO₂ content at 1MHz. The tunability is defined as the percentage change of the relative dielectric constant at 30kV/cm. The tunability of the BSCT thick films increased with decreasing Ca contents because the Curie temperature, as shown in Fig. 3, decreased with increasing Ca contents. The displacement of ions was strongly influenced by the applied fields at around the Curie temperature. The tunability of specimens gradually increased with increasing ZrO₂ contents and the BSCT thick film doped with 2wt% ZrO₂ showed a good value of 15.62% under 30 kV/cm DC bias field. The replacement of Ti⁴⁺ ion (0.068 nm) by larger Zr⁴⁺ ion (0.080 nm) results in a shorter distance between the center ion and its nearest neighbors of the octahedron. This enhances an anharmonic effect [7] and consequently, the tunability increased with an increasing ZrO₂. But, the tunability of the specimens doped with 3 wt% ZrO₂ decreased due to the highly distortion of the unit cell and the internal stress with the decrease of the grain size.

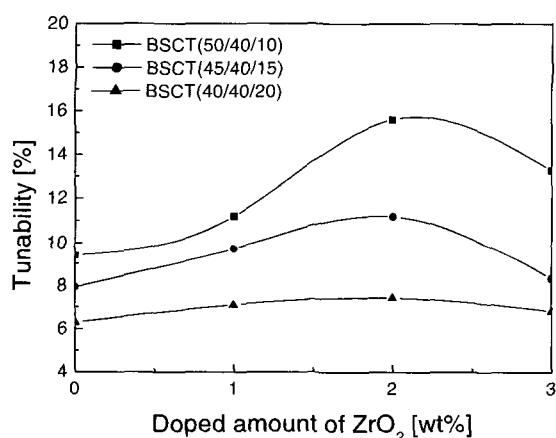


Fig. 6. Tunability of BSCT thick films with various ZrO₂ content at 1MHz.

4. CONCLUSIONS

(Ba,Sr,Ca)TiO₃ powders doped with ZrO₂ were

prepared by sol-gel method and the BSCT thick films were fabricated by the screen printing techniques on alumina substrates. The structural and dielectric properties were investigated with variation of composition ratio and ZrO₂ doping content for microwave phase shifters. All BSCT thick films showed a perovskite polycrystalline structure without a pyrochlore phase. Grain sizes decreased with increasing amounts of ZrO₂. The Curie temperature of BSCT specimens decreased with decreasing Ba/(Sr+Ca) ratio. The relative dielectric constant was non-linearly decreased as the field strength is increased. This is because the applied electric field acts on the non-ferroelectric grains in such a way as to induce a ferroelectric state in these grains. The BSCT(50/40/10) specimen doped with 2 wt% ZrO₂ showed the highest tunability of 15.62% at 30 kV/cm. The tunability of the BSCT specimens was affected by the phase transition temperature and microstructures such as grain size.

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