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Dielectric properties of screen-printed (Ba,Sr,Ca)TiO_3 thick films modified with Al_2O_3 for microwave device applications

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Abstract

(Ba,Sr,Ca)TiO_3 (BSCT) powders, prepared by the sol-gel method, were mixed with organic vehicle and the BSCT thick films were fabricated by the screen printing techniques on alumina substrates. The structural and the dielectric properties were investigated for various composition ratio and Al_2O_3 doping contents. All the BSCT thick films, sintered at 1420°C, showed the typical XRD patterns of a perovskite polycrystalline structure. The thickness of thick films by four-cycle on printing/drying was approximately 95–105 μm. The Curie temperature and relative dielectric constant decreased with increasing Ca content and Al_2O_3 doping amount. The relative dielectric constant, dielectric loss and tunability at 30 kV/cm of the BSCT(50/40/10) thick films doped with 1.0 wt.% Al_2O_3 were 829, 0.39% and 12.94% respectively.

Keywords: Films; Sol-gel processes; Dielectric properties; Perovskite; Tunability; (Ba,Sr,Ca)TiO_3

1. Introduction

Phase controlling components are a key element needed for phased array antennas operating at a fixed frequency. Tuning of the microwave devices can be achieved by both electric and magnetic fields.[1,2] The former employs the dielectric nonlinearity of ferroelectrics, and the latter depends on the nonlinear magnetization of ferrites. Present phased array antennas are constructed from ferrite elements. The ferrite phase shifters require DC current and an induction coil to vary the phase shift and are relatively expensive and complex. Ferroelectric materials, however, require a voltage driven circuit, where the phase shift is caused by a change in the dielectric constant. Since the DC biasing is relatively easy to implement and the power consumption is very low, ferroelectric phase shifters may give much better performance a high power handling capacity, low drive power and low cost compared with ferrite phase shifters. The desired characteristics of dielectric material of choice for phase array applications would be a low dielectric constant, a low dielectric loss and a large tenability.[3] However, the high inherent material loss and high dielectric constant of $BaTiO_3$-system bulk ceramics have restricted its application in phased array antennas. On the other hand, thin or thick films of high dielectric constant ferroelectrics are interesting for planar integrated microwave circuits. But, surface stress in very thin films (<1 μm) results in a significant decrease of the dielectric constant and the tunability and an increase of the dielectric loss compared to bulk $BaTiO_3$-system ceramics. Ferroelectric thick film materials possess merits of bulk materials and thin films. Devices made from thick film not only work 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 study, $BaTiO_3$ powders, partially substituted with Sr^{+2} and Ca^{+2} ions at the A-sites (Ba^{+2} ions) and Al^{+3} ions at the B-sites (Ti^{+4} ions), were prepared by a sol-gel method in order to decrease the phase transition temperature down to below 0 °C and to improve the dielectric properties. (Ba,Sr,Ca)TiO_3 thick films were fabricated by a screen printing method on alumina substrates.

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The structural and dielectric properties were examined for microwave device applications.

2. Experimental

The chemical compositions of the specimens are given by the formula ($Ba_{0.6-x}Sr_{0.4}Ca_x$)TiO_3 (BSCT) + y wt.% Al_2O_3 (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 a mixture of Ba acetate [$Ba(CH_3COO)_2$], Sr acetate hemihydrate [$Sr(CH_3COO)_2 0.5H_2O$], Ca acetate monohydrate [$Ca(CH_3COO)_2H_2O$] and Ti isopropoxide {$Ti(OCH(CH_3)_2)_4$}, were prepared by the sol-gel method. Acetic acid (CH_3COOH) and 2-methoxyethanol ($CH_3OCH_2CH_2OH$) were used as solvents. Ba, Sr and Ca acetate were dissolved in acetic acid, and then the solution was heated 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 2 h in a high purity alumina crucible. After dopant of Al_2O_3 was added to the calcined powders, these powders were mixed and ground by planetary ball milling for 24 h. The ground powder had a particle size ranging from 0.35 to 0.8 μm with the mean diameter of 0.53 μm.

The screen-printable pastes were prepared by kneading the ground BSCT powder with 30 wt.% of organic vehicle (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 20 min. After screen printing the BSCT paste using a 200 mesh screen mask, printed films were allowed to level for 10 min and then dried at 80 °C for 30 min. These processes from printing to drying were repeated four times to obtain a desired thickness. The thick films were sintered at 1420 °C for 2 h in the closed alumina crucible, with an intermediate 2 h 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 30 min.

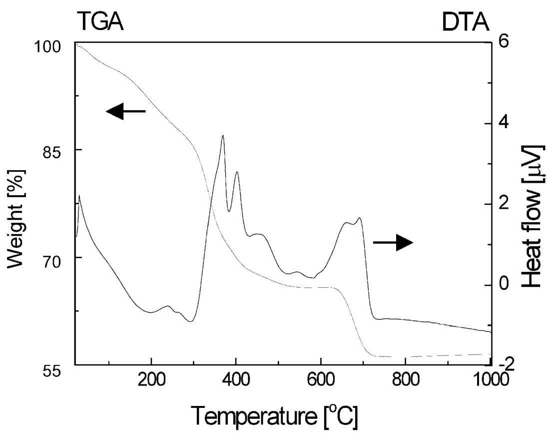

Fig. 1. DTA/TGA curves of the dried BSCT(50/40/10) powders.

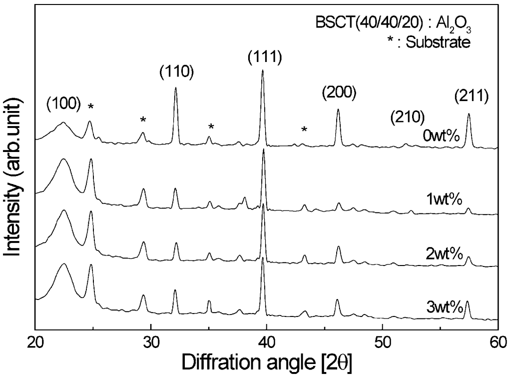

Fig. 2. X-ray diffraction patterns of the Al_2O_3-doped BSCT(40/40/20) thick films sintered at 1420 °C.

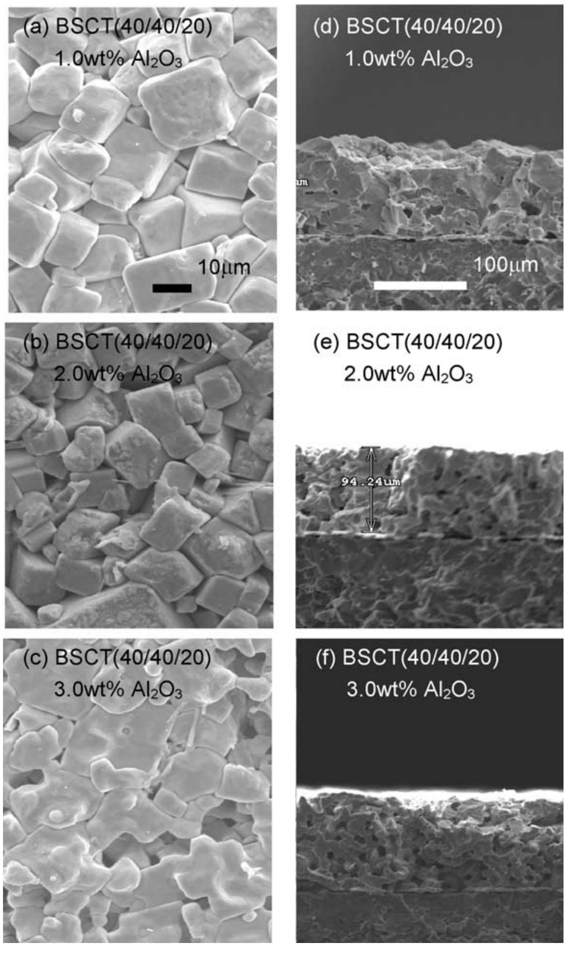

Fig. 3. Surface and cross-sectional SEM micrographs of the BSCT(40/40/20) thick films for various Al_2O_3 contents.

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

Fig. 1 shows the differential thermal analysis (DTA) and the thermogravimetry (TG) curves of the dried BSCT(50/40/10) powders. The weight loss of dried powders derived from the sol-gel method was about 44% at 1000 °C, as determined by the TG curve. An endothermic peak due to the evaporation of absorbed water and solvent were observed at around 200 °C. Due to the combustion of organic residues, exothermic peaks were observed in the temperature range of 350–400 °C. The weight loss at around 700 °C was attributed to the decomposition of barium carbonate, which was formed during heating.[4] Due to the formation of the polycrystalline perovskite phase, exothermic peaks were observed at around 700 °C.

Fig. 2 shows the X-ray diffraction patterns of the Al_2O_3-doped BSCT(40/40/20) thick films printed on alumina substrate. All the BSCT thick films showed the typical XRD patterns of a perovskite polycrystalline structure without a preferred orientation: no pyrochlore

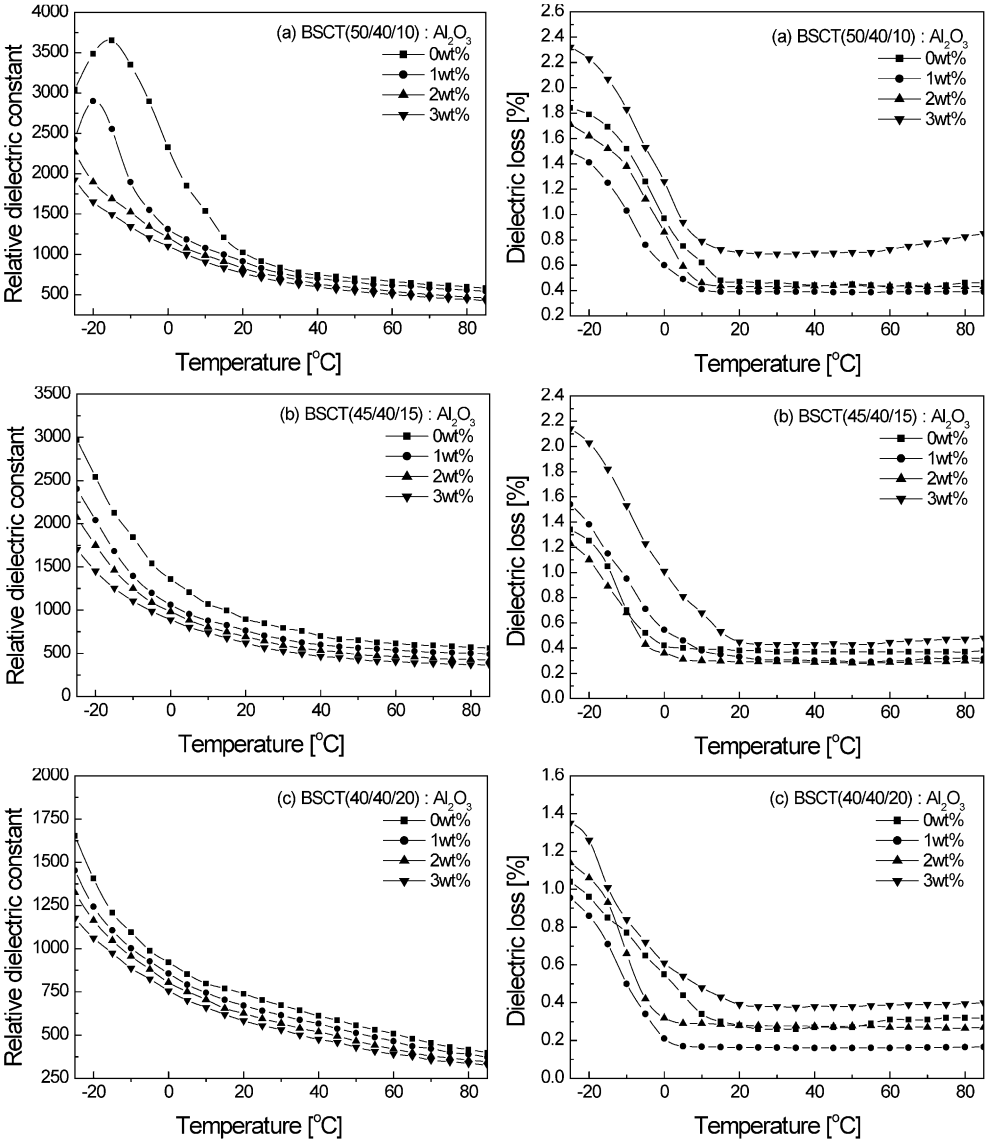

Fig. 4. Relative dielectric constant and dielectric loss as a function of temperature for BSCT thick films with various Al_2O_3 contents.

phase was observed. The lattice constant for the BSCT(50/40/10), BSCT(45/40/15), and BSCT(40/40/20) thick films are 0.3932, 0.3928, and 0.3924 nm, respectively.

Fig. 3 shows the surface and cross-sectional SEM micrographs of the BSCT(40/40/20) thick films printed on Pt/alumina substrate for various Al_2O_3 contents. The grain size decreased with increasing Al_2O_3 amount because a portion of the doping Al ions precipitate out of the normal grains and stay at grain boundaries which subsequently resist the grain growth. The grains of the specimen doped with 3.0 wt.% Al_2O_3 were round, due to deposits of excess Al_2O_3 at grain boundaries in the liquid phase. The average grain size in the BSCT(40/40/20) thick films doped with 1.0 wt.% Al_2O_3 was about 18 μm, and the thickness of all the specimens was approximately 95–105 μm.

Fig. 4 shows the variation of relative dielectric constant and dielectric loss of BSCT thick films as a function of temperature for various Al_2O_3 contents at 1 MHz. The Curie temperature of BSCT specimens decreased with decreasing Ba/(Sr + Ca) ratio. For substitution Sr^{2+}–Ba^{2+}, the bonding force between the A-site ion and the oxygen ion of ABO_3 perovskite structure becomes stronger because the radius of the Ba^{2+} ion (0.135 nm) is larger than that of the Sr^{2+} ion (0.113 nm): the bonding force Ti–O(Sr), therefore, becomes weaker than 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.[5]

The relative dielectric constant and Curie temperature of BSCT thick films decreased with increasing Al_2O_3 amount. These properties may be understood in terms of the effects of the decreasing grain size and the creation of oxygen vacancies. When acceptor ions with a lower positive valence replace metal ions with a higher positive valence in the ABO_3 perovskite structure, oxygen vacancies are created in the lattice, an account of the requirements of electroneutrality. These oxygen vacancies cause a shrinkage of the lattice and affect the transition temperature.[6] The dielectric loss of all specimens was less than 0.01 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 device 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 1.0 wt.% Al_2O_3 were 829 and 0.39%, respectively.

Fig. 5 shows the variation of the relative dielectric constant of BSCT thick films as a function of frequency for various Al_2O_3 contents. The relative dielectric constant decreases in the measured frequency range from 0.5 to 1 GHz and gradually saturates at around 1 GHz. This suggests that the relaxation frequency of the dipolar polarization is about 0.7 GHz for all specimens.

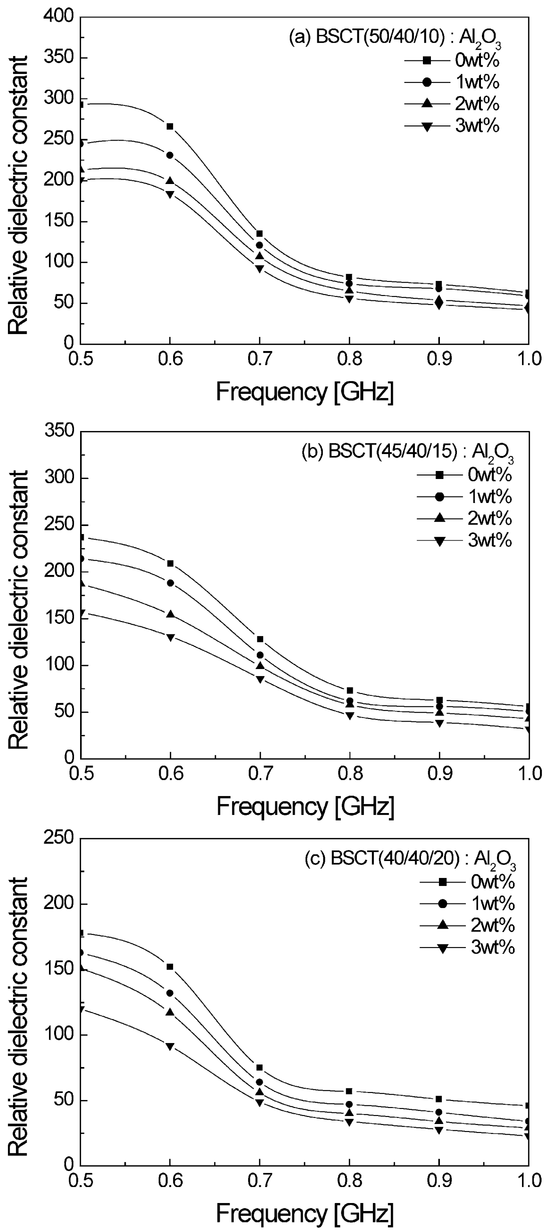

Fig. 5. Relative dielectric constant as a function of frequency for BSCT thick films with various Al_2O_3 contents.

Fig. 6 shows the applied DC field dependence of the relative dielectric constant for BSCT thick films at 1 MHz. The relative dielectric constant of all specimens decreases with increasing the applied DC field. This is because the applied electric fields suppress the displacement of ions inside the grains of paraelectric phase. Also, the non-linear dependence of the dielectric constant on the applied DC electric field results from the chemical inhomogeneities in polycrystalline specimens and/or existence of interfacial layers between the metal electrode and the thick films.[7]

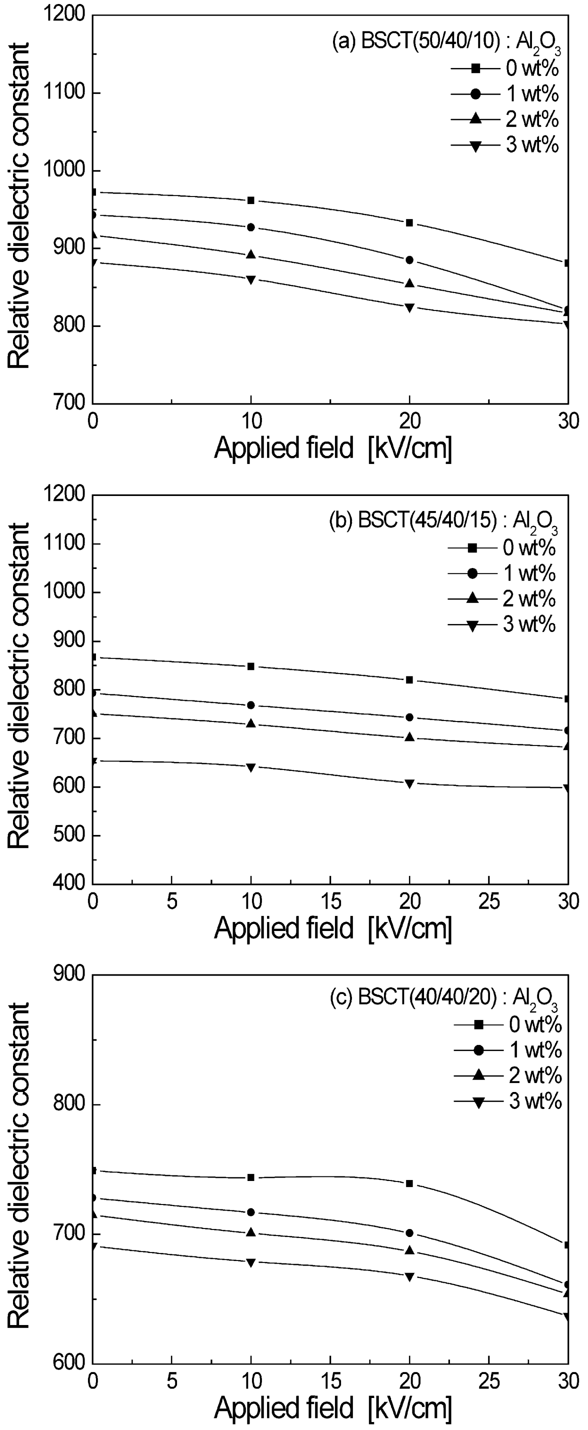

Fig. 6. Relative dielectric constant as a function of the DC electric field for BSCT thick films with various Al_2O_3 contents.

Fig. 7 shows the tunability of BSCT thick films as a function of Al_2O_3 content at 1 MHz. The tunability is defined as the percentage change of the relative dielectric constant at 30 kV/cm. The tunability of the BSCT thick films increases with decreasing Ca contents because the Curie temperature, as shown in Fig. 4, decreased with increasing Ca contents. The BSCT(50/40/10) specimen had the diffused phase transition properties at −15 °C, and the electronic and ionic polarizabilities were strongly influenced by the external fields at around the Curie temperature.[8]

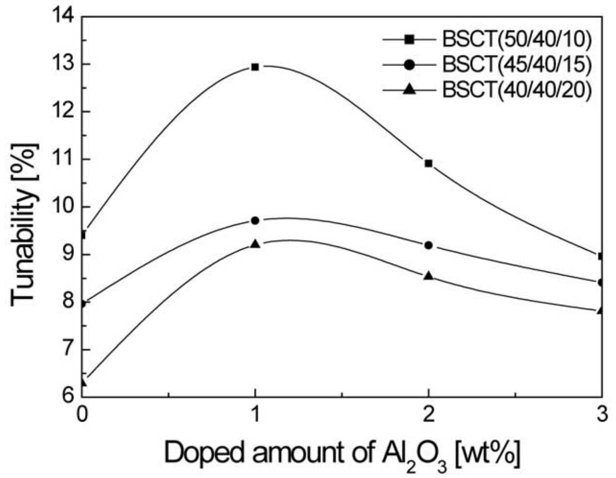

Fig. 7. Tunability of BSCT thick films with various Al_2O_3 content at 1 MHz.

When Al^{3+} ions are substituted for Ti^{4+} ions in BSCT specimens, oxygen vacancies are created in the lattice to satisfy charge neutrality. This results in a shorter distance between the center ions and their nearest neighbors. This enhances the anharmonic effect;[9] consequently, the tunability increases with increasing Al_2O_3 amount. But, the tunability of the specimens doped with more than 2 wt.% Al_2O_3 decreases due to the distortion of the unit cell with an excessive doping and the increasing internal stress with decreasing grain size. The tunability of the BSCT(50/40/10) thick films doped with 1.0 wt.% Al_2O_3 was 12.94% at an electric field of 30 kV/cm.

4. Conclusions

$(Ba,Sr,Ca)TiO_3$ powders doped with Al_2O_3 were prepared by sol-gel method and the BSCT thick films were fabricated by the screen printing techniques on alumina substrates. All BSCT thick films showed a perovskite polycrystalline structure without a pyrochlore phase. The grains of the BSCT specimen doped with 3.0 wt.% Al_2O_3 were round, due to deposits of excess Al_2O_3 at grain boundaries in the liquid phase. The Curie temperature of BSCT specimens decreased with decreasing Ba/(Sr + Ca) ratio. The relative dielectric constant and Curie temperature of BSCT thick films decreased with increasing Al_2O_3 amount. The relative dielectric constant decreases with increase in the applied DC field because the applied electric fields suppress the displacement of ions inside the grains of paraelectric phase. The tunability of the BSCT specimens was affected by the phase transition temperature and microstructures such as grain size.

Acknowledgements

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