Effect of Sintering Temperature on Structural and Dielectric Properties of $(Ba_{0.54}Sr_{0.36}Ca_{0.10})TiO_3$ Thick Films

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Barium strontium calcium titanate powders were prepared with the sol-gel method. Ferroelectric $(Ba_{0.54}Sr_{0.36}Ca_{0.1})TiO_3$(BSCT) thick films were fabricated by the screen-printing method on alumina substrate. Then we investigated the structural and dielectric properties of the BSCT thick films at different sintering temperatures. The thermal analysis showed that the BSCT polycrystalline perovskite phase formed at around 660 °C. The X-ray diffraction analysis showed a cubic perovskite structure with no second phase present in all of the BSCT thick films. The average grain size and the thickness of the specimens sintered at 1450 °C were about 1.6 μm and 45 μm, respectively. The relative dielectric constant increased and the dielectric loss decreased as the sintering temperature was increased; for BSCT thick films sintered at 1450 °C the values of the dielectric constant and the dielectric loss were 5641 and 0.4 %, respectively, at 1 kHz.

Keywords: $(Ba,Sr,Ca)TiO_3$, Thick films, Dielectric constant, Dielectric loss, Provskite

1. INTRODUCTION

During the past decade, there has been an increasing interest in ferroelectric lead zirconate titanate $(Pb(Zr,Ti)O_3)$ and barium titanate $(BaTiO_3)$ films because of their wide range of applications in microelectronics, microelectro-mechanical systems (MEMS), and ultrasonic imaging devices. Potential applications include membrane sensors, micro-accelerometers, and micro motors[1,2]. In general, these devices are based on films with thickness less than 100 μm. Thick-film technologies offer a number of advantages over bulk ceramics for use in ferroelectric micro-system devices. Furthermore, compared with thin-film technology, the thick-film process should allow easier control of both the composition and the homogeneity of complex electronic materials. Thick-film technology using the screen-printing method is most suitable for the preparation of films that are about 10-100 μm in thickness. The screen-printing method makes it possible to perform film preparation and pattern formation simultaneously with little material loss, thus offering high productivity and good cost performance.

Because of their high spontaneous polarization and dielectric properties, $BaTiO_3$ system ceramics have received a great deal of attention for possible application to dynamic random access memories, tunable microwave devices, and various kinds of transducers[3,4]. An even more important property is that the electrical conductivity of $BaTiO_3$ system ceramics can be controlled by a minor modification of the dopants without seriously affecting other properties, ranging from ferroelectricity to semiconductivity. By partially substituting Sr^{2+} and Ca^{2+} ions for Ba^{2+} ions at the A-sites in $BaTiO_3$, one can shift the temperature of the phase transition over a wide range[5]. To date, a number of studies on the $BaTiO_3$ system ceramics have focused on its use as a dielectric in thermistor applications because of the ceramics' high dielectric constant and positive temperature coefficient (PTC).

In this study, we prepared $BaTiO_3$ powders, partially substituted with Sr^{+2} and Ca^{+2} ions at the A-site of the perovskite structure, with the sol-gel method in order to obtain good dielectric properties at the room temperature. Then $BaTiO_3$ system thick films were fabricated by a screen-printing method[8,9]. We investigated the structural and dielectric properties of the BSCT thick films at different sintering temperatures for potential use in various transducers and electronic devices.

2. EXPERIMENTAL PROCEDURE

The $(Ba_{0.54}Sr_{0.36}Ca_{0.1})TiO_3$ (BSCT) powders were prepared with the sol-gel method from Ba acetate $[Ba(CH_3COO)_2]$, Sr acetate $[Sr(CH_3COO)_2{\cdot}0.5H_2O]$, Ca acetate monohydrate $[Ca(CH_3COO)_2{\cdot}H_2O]$ and Ti isopropoxide $\{Ti[OCH(CH_3)_2]_4\}$ as the starting materials and acetic acid (CH_3COOH) and 2-methoxyethanol ($CH_3OCH_2CH_2OH$) as the solvents. The preparation method of the BSCT powders was same as described in a previous paper[6]. Screen-printable pastes were then prepared by kneading the ground BSCT powder with 30 wt% of organic vehicle (Ferro. 75001) in a non-bubbling kneader (NBK-1, Kyoto Electro). High-purity alumina was used as a substrate. The bottom electrodes were prepared screen printing a Pt paste onto the alumina and firing it at 1450 °C for 2 h. After screen printing the BSCT paste with a 200 mesh screen mask, the printed films were allowed to level for 10 min and then dried at 80 °C for 30 min. These processes of printing and drying were repeated six times to obtain the desired thickness. The

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BSCT thick films were sintered at temperatures from 1360 °C to 1450 °C for 2 hr in a closed alumina crucible.

The dried powders were examined by thermo gravimetric analysis (TGA)/differential thermal analysis (DTA). We used X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM) to analyze the crystallinity and microstructures of the thick films. For our dielectric measurements, we fabricated the upper electrodes with screen printing Ag paste and then firing at 590 °C for 10 min. The electrical properties of the specimens were measured using an LCR-meter and an electrometer. Figure 1 shows the flow chart for the fabrication of the BSCT thick films with the screen-printing method.

3. RESULTS AND DISCUSSION

Figure 2 shows the differential thermal analysis (DTA) and the thermogravimetry (TG) curves for the dried BSCT(54/36/10) powders. The dried powders derived from the sol-gel method had lost about 42 % of their weight at 1000 °C, as determined by the TG curve. An endothermic peak produced by the evaporation of absorbed water and solvent was observed in the temperature range of 100 °C to 350 °C. The combustion of organic residues produced exothermic peaks at around 400 °C. The weight loss in the temperature range of 600 °C to 700 °C was attributed to the decomposition of barium carbonate, which was formed during heating[7]. The exothermic peak observed at around 660 °C was due to the formation of the polycrystalline perovskite phase.

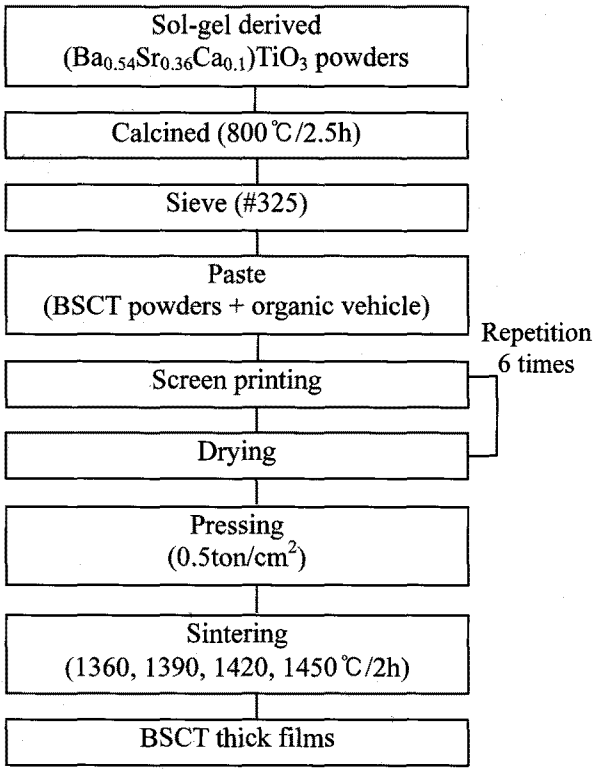

Fig. 1. Flow chart for the fabrication of BSCT thick films.

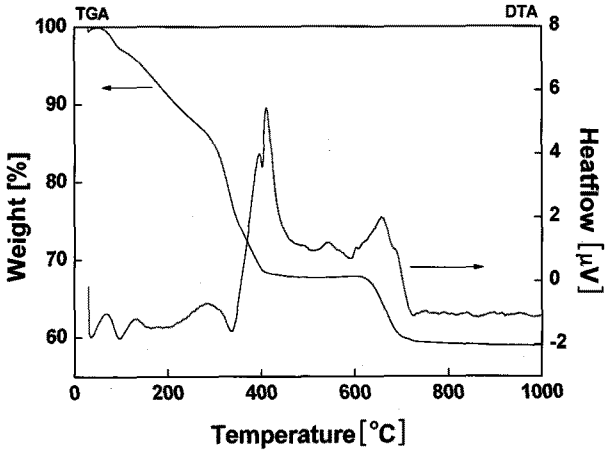

Fig. 2. DTA/TGA curves for the dried BSCT powders.

Figure 3 shows the X-ray diffraction patterns of the BSCT thick films prepared at different sintering temperatures. All the BSCT thick films showed the typical XRD patterns of a cubic polycrystalline structure. The results also clearly show no diffraction peaks from impurity phases, indicating that the films have a high degree of crystallinity. The lattice constant was calculated by Bragg's law and inter-plane spacing equation. The lattice constant of the BSCT(54/36/10) specimens was 0.3952 nm, and it did not change as the sintering temperature was varied.

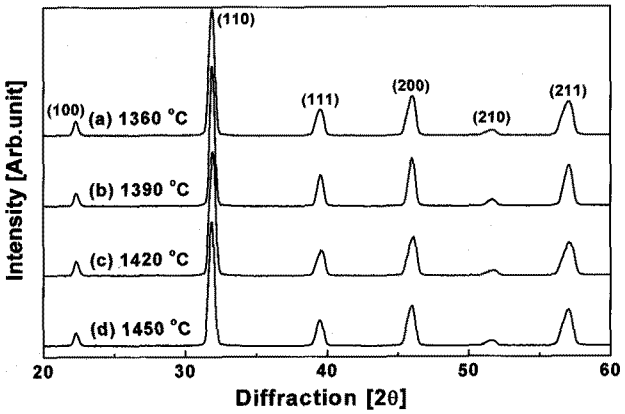

Fig. 3. XRD patterns of BSCT thick films prepared at different sintering temperatures.

Figure 4 shows the surface FE-SEM micrographs of the BSCT thick films prepared with different sintering temperatures. All the BSCT thick films adhered to the Pt/alumina substrate without cracking and exfoliation, and they all had a relatively flat surface and were composed of grains with relatively uniform size. The BSCT thick film sintered at 1360 °C had a porous structure, but the porosity at the surface and inside the films decreased as the sintering temperature was increased. The average grain size and thickness of the BSCT thick films sintered at 1450 °C were approximately 1.6 μm and 45 μm, respectively.

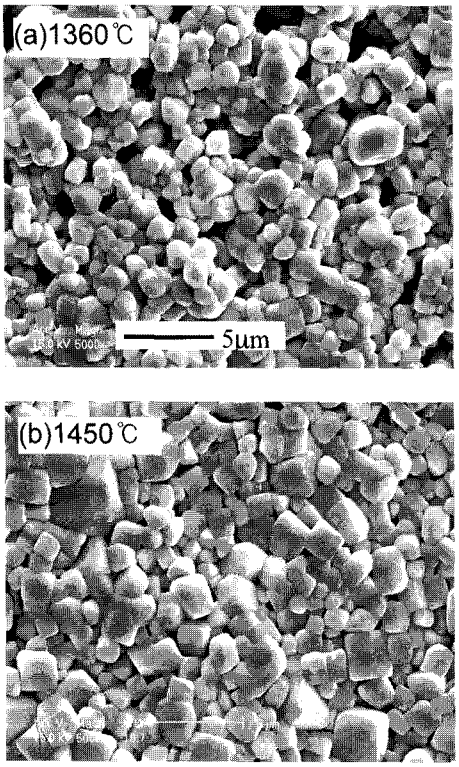

Fig. 4. Surface FE-SEM micrographs of the BSCT thick films prepared at different sintering temperatures.

Figure 6 shows the current densities of the BSCT thick films prepared at different sintering temperatures. The leakage current densities decreased at the sintering temperatures were increased because of the increase in surface densification and the reduction the porosity. In all thick films the leakage current densities were less than 10^{-9} A/cm^2 at the applied electric field range of 0-20 kV/cm.

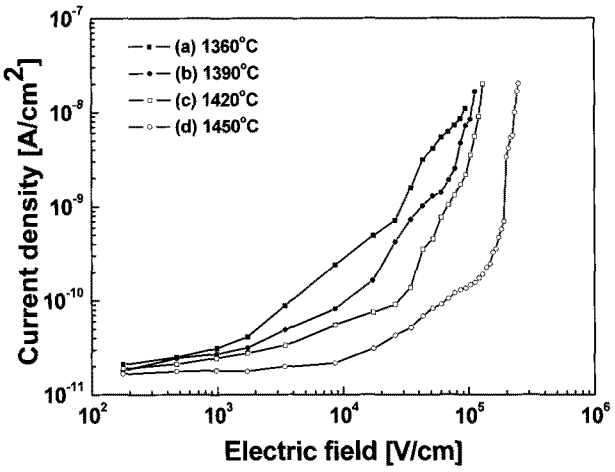

Fig. 6. Current densities of BSCT thick films prepared at different sintering temperatures.

Figure 5 shows the relative dielectric constant and dielectric loss of BSCT thick films prepared at different sintering temperatures, measured at 1 kHz. The relative dielectric constant increased, and the dielectric loss decreased as the sintering temperature was increased; the values for BSCT thick films sintered at 1450 °C were 5641 and 0.4 %, respectively. This pattern can be explained by the increase in the density and grain size and the reduction of the porosity as the sintering temperature is increased. For all samples the dielectric loss was less than 0.01 at room temperature. This small value is sufficient for application in various electronic devices.

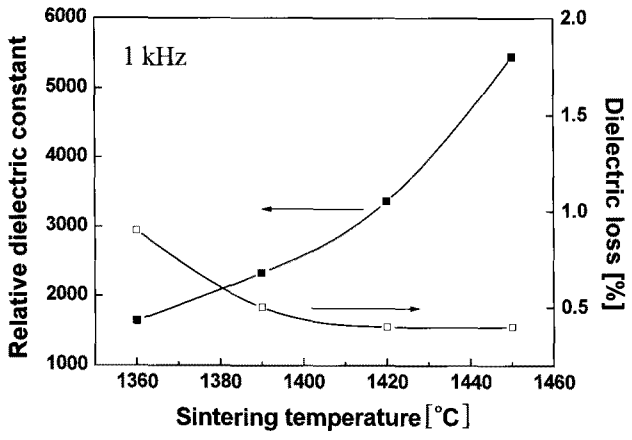

Fig. 5. Relative dielectric constant and dielectric loss of BSCT thick films (at 1 kHz) prepared at different sintering temperatures.

4. CONCLUSION

We prepared $(Ba_{0.54}Sr_{0.36}Ca_{0.1})TiO_3$ (BSCT) powders with the sol-gel method from a solution of Ba, Sr, and Ca acetate and Ti isopropoxide. The BSCT thick films were screen printed on high-purity alumina substrates, and we investigated the structural and dielectric properties of BSCT thick films prepared at different sintering temperatures. We observed the formation of the polycrystalline BSCT phase at around 660 °C. All BSCT thick films showed the typical XRD patterns of a cubic polycrystalline structure. The BSCT thick film sintered at 1360 °C had a porous structure, but the porosity at surface and inside of the films decreased as the sintering temperature was increased. The relative dielectric constant and dielectric loss of the BSCT thick films sintered at 1450 °C were about 5641 and 0.4 %, respectively, when measured at 1 kHz. The leakage current densities decreased as the sintering temperature was increased because of the increase in surface densification and the reduction in the porosity.

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