Electrical Properties of $BaTiO_3$ Thick Films Fabricated by Screen-printing Method

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$(Ba_{0.6}Sr_{0.3}Ca_{0.1})TiO_3$ (BSCT) thick films doped with 0.1 mol% $MnCO_3$ and Yb_2O_3 (0.1~0.7 mol%) were fabricated by the screen printing method on the alumina substrates. And the structural and electrical properties as a function of Yb_2O_3 amount were investigated. The exothermic peak was observed at around 680 °C due to the formation of the polycrystalline perovskite phase. The lattice constants of the BSCT thick film doped with 0.7 mol% is 0.3994 nm. The specimen doped with 0.7 mol% Yb_2O_3 showed dense and uniform grains with diameters of about 4.2 μm. The average thickness of all BSCT thick films was approximately 70 μm. Relative dielectric constant and dielectric loss of the specimen doped with 0.7 mol% Yb_2O_3 were 2823 and 3.4 %, respectively. The Curie temperature of the BSCT thick films doped with 0.1 mol% Yb_2O_3 was 46 °C.

Keywords : $BaTiO_3$, Thick films, Ferroelectric, Screen printing

1. INTRODUCTION

Perovskite based materials are widely used in technical applications. Multilayer ceramic capacitor (MLCC), semiconductors with positive temperature coefficient of resistance (PTCR) and pyroelectric detectors are some of the versatile possibilities of applications[1,2]. $BaTiO_3$ is one of the most used dielectric materials and therefore often an object of research. Doped $BaTiO_3$ and solid solutions with e.g. $SrTiO_3$ provide new properties of ceramic materials. In particular, the polarization and dielectric constant change rapidly near the cubic-tetragonal $BaTiO_3$ phase transition, which makes this the most sensitive operation regime to defect infrared radiation. By partially substitution Sr^{2+} and/or Ca^{2+} ions at A-sites (Ba^{2+} ions) in $BaTiO_3$, one can set the temperature of the phase transition over a wide range[3].

For the last twenty years, screen-printing technology has been applied extensively in a variety of fields, especially microelectronics. The manufacture of hybrid circuits, as well as the fabrication of the discrete components used in surface mounting technology, takes advantage of this thick-film technology. Generally, thick films obtained by screen-printing technology are expected to be more cost effective than lapped bulk ceramics. Moreover, compared to thin-film technology, the screen-printing process should allow easier control of both the composition and the homogeneity of complex ferroelectric ceramics. The thick film technology using the screen printing method is the most suitable for the preparation of films of about 10~100 μm thickness. Screen printing method offers simultaneous process for films preparation and pattern formation with little material loss. Therefore, it offers high productivity and good cost performance.

A large number of rare earth additives have been successfully incorporated in the ABO_3 perovskite system of the ferroelectric ceramics to tailor the properties of these ceramics. In this study, $BaTiO_3$ powders, partially substituted with Sr^{+2} and Ca^{+2} ions at the A-site (Ba^{+2} ions) of the perovskite structure were prepared by sol-gel method in order to decrease the phase transition temperature to below room temperature and to produce specimens with more stable dielectric properties at the room temperature. And $(Ba,Sr,Ca)TiO_3$ thick films were fabricated by a screen-printing method. The dependences of the structural and dielectric properties on the Yb_2O_3 content were examined.

2. EXPERIMENTAL

The chemical compositions of the specimens were given according to the following formula: $(Ba_{0.6}Sr_{0.3}Ca_{0.1})TiO_3$ + 0.1 mol% $MnCO_3$ + x mol% Yb_2O_3 (x= 0.1, 0.3, 0.5, 0.7). This BSCT composition gave a transition temperature below room temperature. BSCT powders, started with a mixture of Ba acetate ($Ba(CH_3COO)_2$), Sr aceteate ($Sr(CH_3COO)_2 \cdot 0.5H_2O$), Ca aceteate ($Ca(CH_3COO)_2 \cdot H_2O$) and Ti isopropoxide ($Ti[OCH(CH_3)_2]_4$) were prepared by the sol–gel method. Acetic acid and 2-methoxyethanol ($CH_3OCH_2CH_2OH$) were used as solvents. Ba, Sr, and Ca acetates were dissolved in acetic acid, and then the solution was heated to 115 °C for the evaporation of water. After cooling, Ti-isopropoxide, dissolved in 2-methoxyethanol, was added to the solution. The solution temperature was maintained at 60 °C during refluxing. The powder precursors were dried and then calcined in a high-purity alumina crucible.

After dopant of 0.1 mol% $MnCO_3$ and Yb_2O_3 were added to the calcined powders, these powders were mixed and ground by planetary ball milling for 24 h. The screen-printable pastes were prepared by kneading the ground BSCT powder with 30 wt% of organic vehicle (Ferro. 75001). High purity alumina was used as a substrate. The bottom electrodes were prepared by screen printing method with Pt paste and firing at 1450 °C for 20 min. After screen printing, printed films were dried and these processes of printing and drying were repeated 6-times to obtain a desired thickness. The coated thick films were sintered at 1420 °C for 2 h in the closed alumina crucible.

The crystalline phase was identified by an X-ray diffractometry (Bruker, AXS D8 DISCOVER with GADDS, Germany). The surface and cross-sectional microstructure were examined by a field emitting scanning electron microscope (Philips, XL30 S FEG, Netherland). The average grain size was determined by the lineal intercept method. The dielectric properties of the thick films were measured using LCR-meter (Fluke, PM6306, Germany).

3. RESULTS AND DISCUSSION

Figure 1 shows the differential thermal analysis (DTA) and the thermogravimetry (TG) curves of the dried BSCT(60/30/10) 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. Endothermic peaks due to the evaporation of absorbed water and solvent were observed in the temperature range of 100 °C to 350 °C. Due to the combustion of organic residues, exothermic peaks were observed at around 420 °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[4]. The exothermic peak was observed at around 680 °C due to the formation of the polycrystalline perovskite phase.

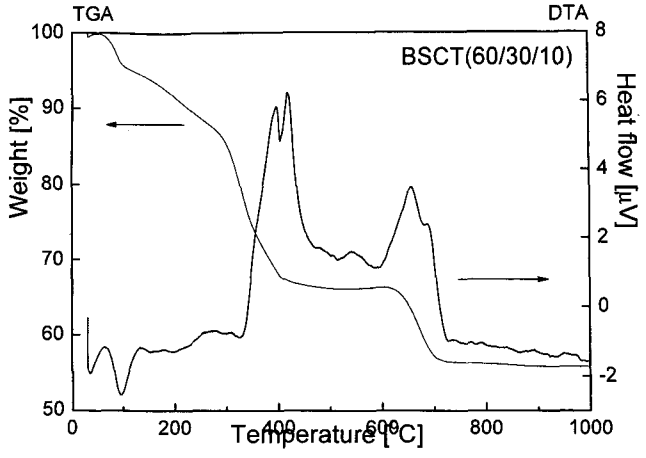

Fig. 1. DTA/TGA curves of the dried BSCT(60/30/10) powders.

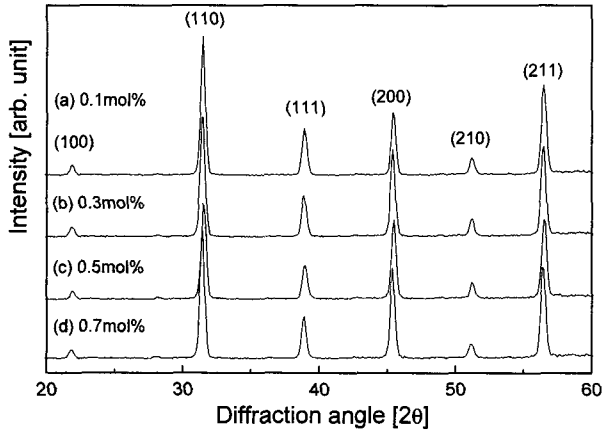

Fig. 2. X-ray diffraction patterns of the BSCT thick films as a function of Yb_2O_3 amount.

Figure 2 shows X-ray diffraction patterns of the BSCT thick films as a function of Yb_2O_3 amount. All BSCT thick films showed the typical XRD patterns of cubic perovskite polycrystalline structure and no pyrochlore phase was observed. The lattice constants of BSCT specimens were independent of the Yb_2O_3 contents. This can probably be explained by the fact that the Yb^{3+} ions irregularly substituted for Ba^{2+}, Sr^{2+} and Ca^{2+} ions at the A-sites of ABO_3 perovskite structure. The lattice constants of the BSCT thick film doped with 0.1 mol%, 0.5 mol% and 0.7 mol% Yb_2O_3 are 0.3987 nm, 0.3987 nm and 0.3994 nm, respectively.

The particle size distribution was measured by using a particle size analyzer (UPA-150, USA). The particle size distribution of the calcined BSCT powder is shown in Fig. 3. The sol-gel derived PZT powders exhibited a broad distribution with mean particle size of about 1 μm.

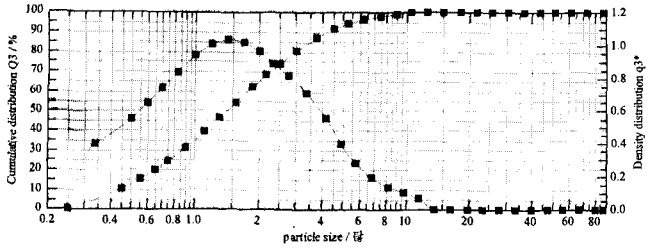

Fig. 3. Particle-size distribution of the BSCT powder derived from the sol-gel method.

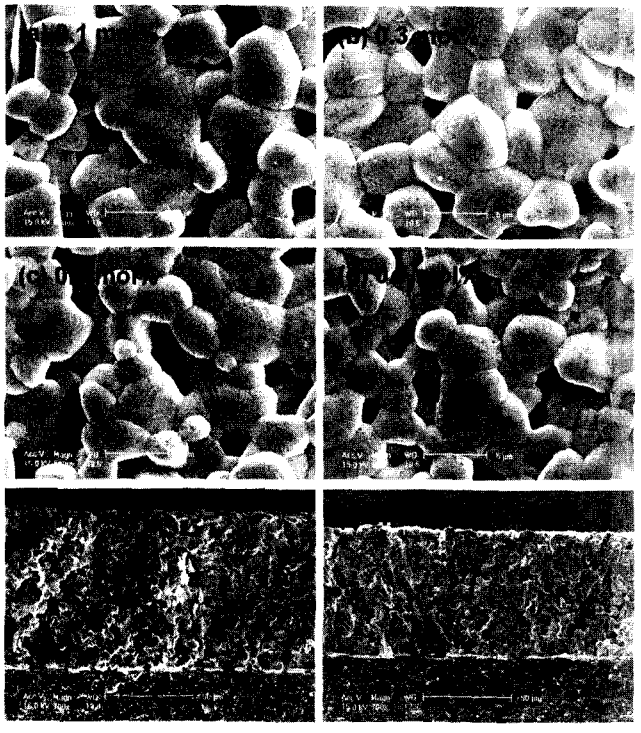

Fig. 4. Surface and cross-sectional SEM micrographs of BSCT thick films as a function of Yb_2O_3 amount.

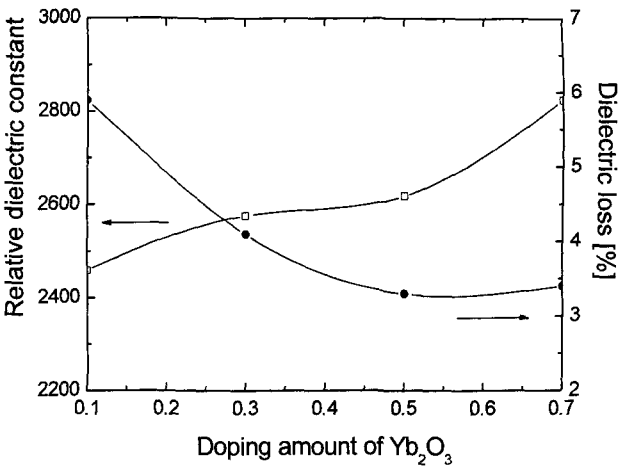

Fig. 5. Relative dielectric constant and dielectric loss of the BSCT thick films as a function of Yb_2O_3 amount at room temperature.

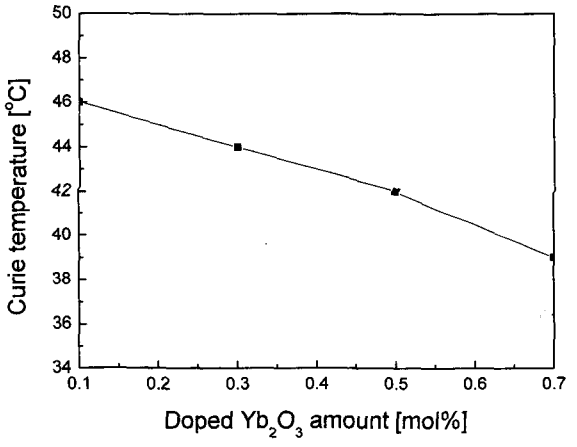

Fig. 6. Curie temperature of BSCT thick films as a function of Yb_2O_3 amount.

Figure 4 shows surface and cross-sectional SEM micrographs of BSCT thick films as a function of Yb_2O_3 amount. The densification increased and average grain size decreased with increasing the Yb_2O_3 amount. These are due to the fact that Yb^{3+} ions act on the donor dopant in the BSCT specimens[5]. The specimen doped with 0.7 mol% Yb_2O_3 showed dense and uniform grains with diameters of about 4.2 μm. The thickness of the BSCT thick films was approximately 70 μm.

Figure 5 shows relative dielectric constant and dielectric loss of BSCT thick films as a function of Yb_2O_3 amount at 1 kHz. The relative dielectric constant increased and dielectric loss decreased with increasing the Yb_2O_3 contents. These properties may be understood in terms of the effects of decreasing the Curie temperature with the highest value to room temperature, as shown in Fig. 6, and increasing the densifications. Relative dielectric constant and dielectric loss of the specimen doped with 0.7 mol% Yb_2O_3 were 2823 and 3.4 %, respectively.

Figure 6 shows the Curie temperature of BSCT thick films as a function of Yb_2O_3 amount at 1 kHz. The Curie temperature of BSCT specimen decreased with increasing the content of Yb_2O_3 because Yb^{+3} ions created cation vacancies in the lattice which is used for the maintenance of electroneutrality[6]. The Curie temperature of the BSCT thick films doped with 0.1 mol% and 0.7 mol% were 46 °C and 39 °C, respectively.

Figure 7 shows relative dielectric constant of BSCT thick films at room temperature as a function of frequency for the various Yb_2O_3 amount. The relative dielectric constant slowly decreased with increasing the applied frequency and all BSCT specimens showed the typical dielectric dispersion properties[7].

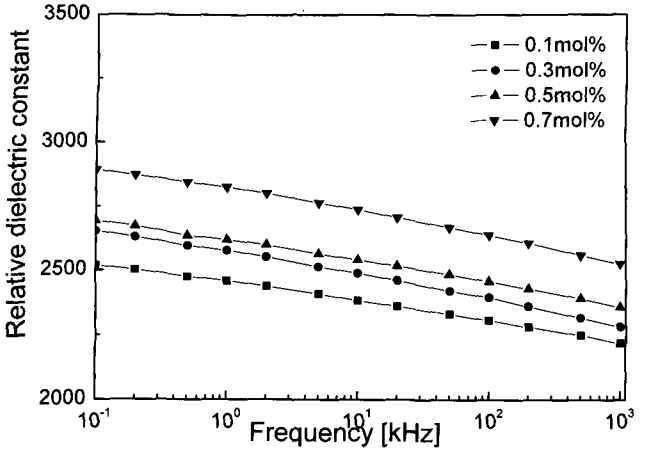

Fig. 7. Relative dielectric constant of BSCT thick films as a function of frequency.

4. CONCLUSION

In this research, BSCT thick films doped with $MnCO_3$ (0.1mol%) and Yb_2O_3 (0~0.7 mol%), were fabricated by the screen-printing method. All BSCT thick films showed the typical XRD patterns of cubic perovskite polycrystalline structure. The densification increased and average grain size decreased with increasing the Yb_2O_3 amount. The average thickness of BSCT thick films was approximately 70 μm. The relative dielectric constant increased and dielectric loss decreased with increasing the Yb_2O_3 contents. These properties may be understood in terms of the effects of decreasing the Curie temperature with the highest value to room temperature and increasing the densifications. Relative dielectric constant and dielectric loss of the specimen doped with 0.7 mol% Yb_2O_3 were 2823 and 3.4 %, respectively. The Curie temperature decreased with increasing Yb_2O_3 amount because Yb^{+3} ions created cation vacancies in the lattice which is used for the maintenance of electroneutrality. The Curie temperature of the BSCT thick film doped with 0.7 mol% was 39 °C. All BSCT specimens showed the typical dielectric dispersion properties.

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