Influence of Yb_2O_3 Doping Amount on Screen-printed Barium Strontium Calcium Titanate Thick Films

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$(Ba_{0.9-x}Sr_xCa_{0.10})TiO_3$ (x=0.33, 0.36) powders were prepared by sol-gel method. (Ba,Sr,Ca)TiO_3 (BSCT) thick films, undoped and doped with $MnCO_3$ and Yb_2O_3 (0.1~0.7 mol%), were fabricated by the screen printing method on the alumina substrate. The coating and drying procedure was repeated 6-times. The Pt bottom electrode was screen printing method on the alumina substrate. These BSCT thick films were annealed at 1420 °C for 2 hr in atmosphere. The upper electrodes were fabricated by screen printing the Ag paste and then firing at 590 °C for 10 min. And then the structured and dielectric properties as a function of the doping amount of Yb_2O_3 were studied. As a result of the TG-DTA, exothermic peak was observed at around 670 °C due to the formation of the polycrystalline perovskite phase. All BSCT thick films showed XRD patterns of typical cubic peroveskite structure. The average thickness of BSCT thick films was about 70 μm. The curie temperature and the dielectric constant decreased with increasing Yb_2O_3 doped content and the relative dielectric constant of the specimen, doped with 0.5 mol% Yb_2O_3 at BSCT(54/36/10), showed a best value of 5018 at curie temperature.

Keywords : BSCT, Dielectric, Thick film, Curie temperature, Screen-printing

1. INTRODUCTION

Recently, ferroelectric materials have attracted considerable attentions due to their chemical stability, high permittivity and low loss. Among which, barium strontium calcium titanate ((Ba,Sr,Ca)TiO_3, BSCT) is becoming more attractive because of its high dielectric constant and large dielectric breakdown strength compared to $BaTiO_3$, $PbTiO_3$[1-5].

In general, $BaTiO_3$, $SrTiO_3$, and $CaTiO_3$ are the representative ABO_3-type perovskite materials. $BaTiO_3$ is usually a ferroelectric material with the Curie temperature of 120 °C. $SrTiO_3$ is a paraelectric one with no ferroelectric phase transition[4]. (Ba,Sr,Ca)TiO_3 simultaneously has the advantages of high dielectric constant of $BaTiO_3$ and the structural stability of $SrTiO_3$ [4-6]. In view of their merits, the investigation on BSCT solid solution is therefore significantly important[3-7].

Generally, by altering the cation composition in ABO_3 ferroelectric ceramics, one can set the temperature of the phase transition over a wide range. In addition, the electrical property of these ceramics can be controlled by minor modification of the dopants without serious affecting other properties[8]. In this paper, $BaTiO_3$ ceramics, partially substituted with Sr^{2+} and Ca^{2+} ions at A-site(Ba^{2+} ions), were prepared by the mixed oxide method in order to decrease the to improve the densification and dielectric properties. The structural and the dielectric properties as functions of the composition ratio and doped Yb_2O_3 amounts were investigated for dielectric and pyroelectric applications.

2. EXPERIMENT

The chemical compositions of the samples were given according to the following formula: $(Ba_xSr_{0.9-x}Ca_{0.1})TiO_3$ (x= 0.54, 0.57) + 0.1 mol% $MnCO_3$ + y mol% Yb_2O_3 (y= 0.1, 0.3, 0.5, 0.7). This $(Ba_xSr_{0.9-x}Ca_{0.1})TiO_3$ (BSCT) composition gave a transition temperature near the

ambient room temperature. Doped BSCT specimens with 0.1 mol% $MnCO_3$ were selected for their basic composition on the basis of previous experiments. BSCT powders, started with a mixture of Ba acetate [$Ba(CH_3COO)_2$], Sr acetaten hemihydrate [$Sr(CH_3COO)_2$,$0.5H_2O$], Ca acetate monohydrate [$Ca(CH_3COO)_2$,H_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. In the initial stage, Ba, Sr, and Ca acetates were dissolved in acetic acid with a molar ratio of 1 : 17 at 90 °C, and then the solution was heated to 115 °C for the evaporation of water. After cooling to 60 °C, Ti-isopropoxide, dissolved in 2-methoxyethanol, was added to the solution. This mixed solution was refluxed for 1 h, and then water and 2-methoxyethanol were added to the solution for stabilization and hydrolysis, respectively. The solution temperature was maintained at 60 °C during refluxing. The powder precursors were dried slowly at 100 °C for 72 h and then calcined at 800 °C for 2 h in a high-purity alumina crucible. After dopants of Yb_2O_3 and $MnCO_3$ were added to the calcined BSCT powders, these powders were mixed and ground for 24 h with ZrO_2 grinding media in acetone solution. 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 Pt paste and firing at 1450 °C for 2 hr. 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 of printing and drying were repeated 6-times to obtain a desired thickness. The coated thick films were sintered at 1450 °C for 2 h in the closed alumina crucible. The thermal decomposition of the sols, dried at 100 °C, was followed by simultaneous thermal analysis thermogravimetry and differential thermal analysis (TA, SDT Q600, USA). The crystalline phase was identified by an X-ray diffractometry (Bruker, AXS D8 DISCOVER with GADDS, Germany). The surface and cross-sectional microstructure was examined by a field emitting scanning electron microscope (Philips, XL30 S FEG, Netherland).The average grain size (d) was determined by the lineal intercept method as follow:

$$d = \frac{1.56L}{MN}$$

Where L is the random line length on the micrograph, M is the magnification of the micro graph, and N is the number of the grain boundaries intercepted by lines[9].

For the electrode formation, fired-on silver paste was used on both surfaces of the specimens. The dielectric properties of the specimens were measured suing LCR-meter (Fluke, PM6306, Germany). Relative dielectric constant and dielectric loss as function of temperature were measured using LCR meter and thermostatic chamber (Delta design, Delta 9023, USA).

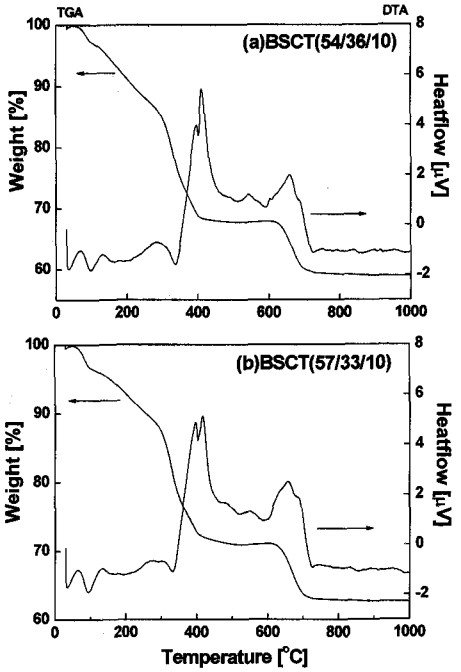

Fig. 1. TG-DTA curve of BSCT(54/36/10) powder and BSCT(57/33/10) powder. (a) BSCT(54/36/10) powder, (b) BSCT(57/33/10) powder.

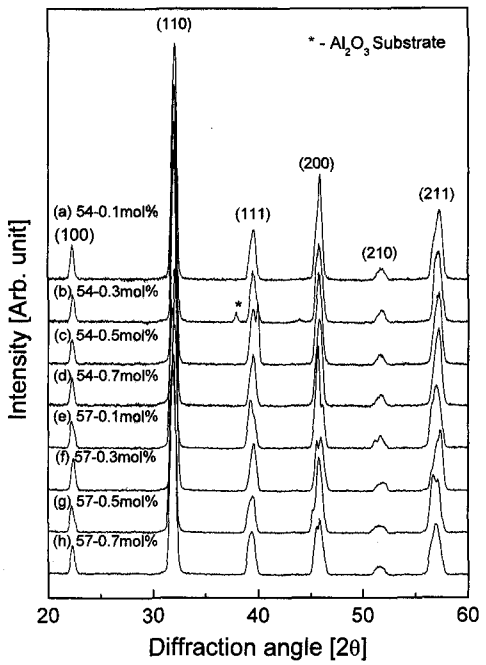

Fig. 2. X-ray diffraction patterns of the BSCT thick films as a function of doped Yb_2O_3 amount.

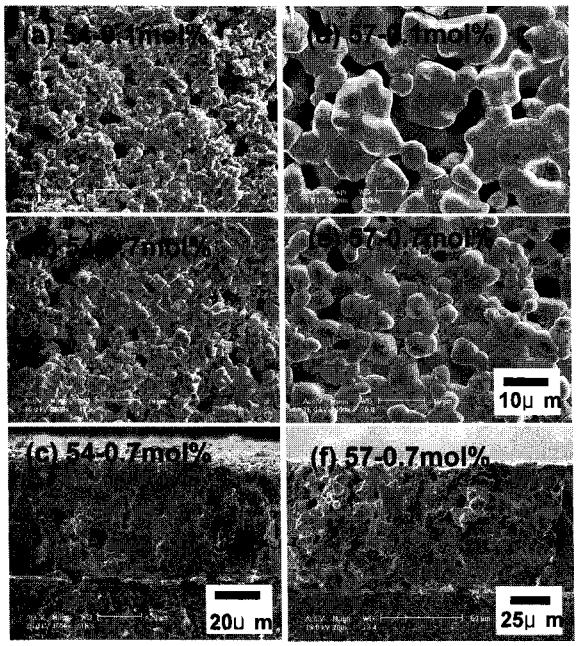

Fig. 3. Surface and SEM micrographs of the BSCT thick films as a function of doped Yb_2O_3 amount.

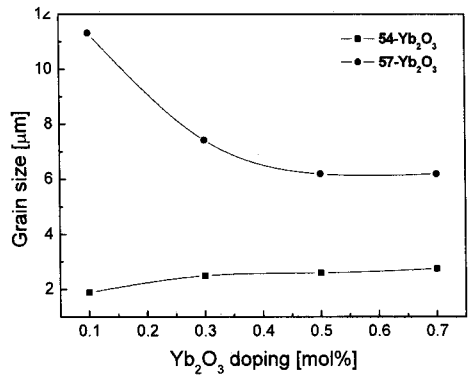

Fig. 4. Average grain size of the BSCT thick films as a function of doped Yb_2O_3 amount.

3. RESULTS AND DISCUSSION

Figure 1 shows the thermogravimetry and differential thermal analysis (TG-DTA) curves of the dried BSCT(54/36/10) powders and BSCT(57/33/10) powders. The weight loss of dried powders derived from the sol-gel method was about 35~40 % 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 300 °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

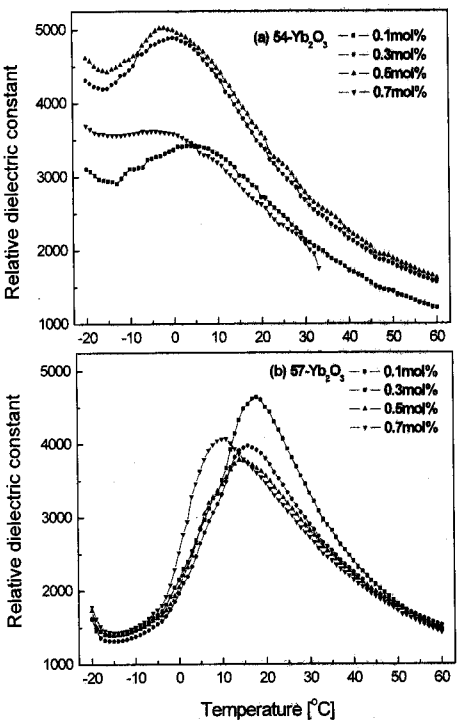

Fig. 5. Relative dielectric constant of BSCT thick films as function of temperature and doped Yb_2O_3 amount at 1 kHz. (a) BSCT(54/36/10)-Yb_2O_3, (b) BSCT(57/33/10)-Yb_2O_3.

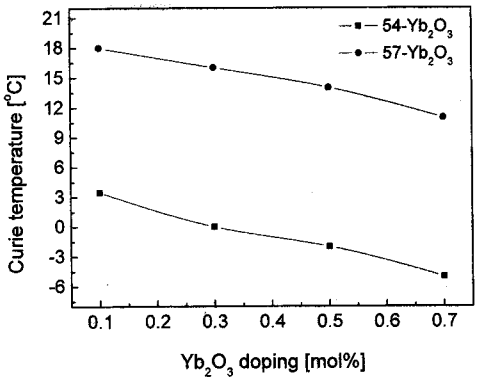

Fig. 6. Curie temperature of BSCT thick films as function of doped Yb_2O_3 amount at 1 kHz.

barium carbonate, which was formed during heating. Due to the formation of the polycrystalline perovskite phase, exothermic peaks were observed at around 700 °C.

Figure 2 shows X-ray diffraction patterns of the BSCT thick films as a function of doped 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 constant of BSCT specimens decreased with increasing Sr content, because the radius of the Sr^{2+} ion (0.127 nm) is smaller

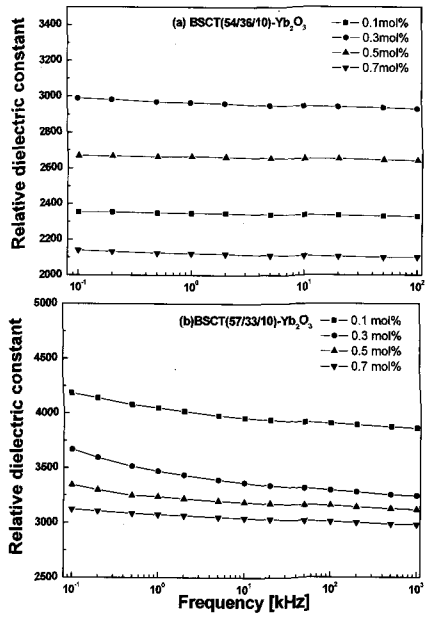

Fig. 7. Relative dielectric constant of BSCT thick films as function of frequency and doped Yb_2O_3 amounts. (a) BSCT(54/36/10)-Yb_2O_3, (b) BSCT(57/33/10)-Yb_2O_3.

than that of the Ba^{2+} ion (0.143 nm). The values of the BSCT(54/36/10) and BSCT(57/33/10) thick films are 0.394 and 0.396, respectively.

Figure 3 shows surface SEM micrographs of the BSCT thick films as a function of doped Yb_2O_3 amount. The densification increased with the increasing the Yb_2O_3 amount. The BSCT(54/36/10) and BSCT (57/33/10) thick films doped with 0.6 mol% Yb_2O_3 exhibited a dense and uniform grain structure. The average thickness of the BSCT(54/36/10) and BSCT (57/33/10) thick films were 60 μm and 70 μm, respectively.

Figure 4 shows average grain size of the BSCT thick films as a function of doped Yb_2O_3 amount. The average grain size of BSCT(54/36/10) thick films increasing with the increasing Yb_2O_3 amount. But the average grain size of BSCT(57/33/10) thick films decreased with the increasing Yb_2O_3 amount. The average grain size of the BSCT(54/36/10)-0.1 mol% and BSCT(57/33/10)-0.7 mol% thick films are 1.89 μm and 6.32 μm, respectively.

Figure 5 and Fig. 6 show relative dielectric constant and curie temperature of BSCT thick films as function of temperature and doped Yb_2O_3 amounts at 1 kHz. The relative dielectric constant and the curie temperature of BSCT thick films decreased with the Yb_2O_3 amount. These properties may be understood in terms of the second phase at grain boundaries. Also, the lower charge on the B-site cations in the ABO_3 perovskite structure is compensated for by vacant oxygen sites which shrinks the lattice and affects the transition temperature[10]. The curie temperature of BSCT thick films decreased with the decreasing Ba/Sr ratio. For substitution Sr^{2+}-Ba^{2+}, the bonding force between the A-site ion is larger than that of the Sr^{2+} ion(0.127 nm) the bonding force Ti-O(Sr) 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[11].

Figure 7 shows relative dielectric constant of BSCT thick films as function of frequency and doped Yb_2O_3 amount. The relative dielectric constant decreased with an increased with an increase the applied frequency and the BSCT thick films showed the typical dielectric dispersion properties. The relative dielectric constant of BSCT(57/33/10) thick films increased with increasing the Yb_2O_3 amount. However, relative dielectric constant of BSCT(54/36/10) thick films was the low be reduced gradually after the increase. It can be understood in terms of the effect of increment of the curie temperature shifter with Yb_2O_3 doping.

4. CONCLUSION

In this research, BSCT thick films doped with $MnCO_3$ (0.1 mol%) and Yb_2O_3, were fabricated by the screen-printing method. BSCT powders were prepared by sol-gel method using a solution of Ba, Sr and Ca acetate in acetic acide, 2-methoxyethanol and Ti iso-propoxide solution. The formation of the polycrystalline perovskite phase, exothermic peaks were observed at around 700 °C. All BSCT thick films showed a perovskite polycrystalline structure without a pyrochlore phase. The densification increased with the increasing the Yb_2O_3 amount. The average grain size of the BSCT(54/36/10)-0.1 mol% and BSCT(57/33/10)-0.7 mol% thick films are 1.89 μm and 6.32 μm, respectively. The relative dielectric constant and the curie temperature of BSCT thick films decreased with the Yb_2O_3 amount. The curie temperature of BSCT thick films decreased with decreasing Ba/Sr ratio.

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