

Influence of Dy_2O_3 doping amount on barium strontium carciun titanate thick films by screen-printing method

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$(Ba_{0.57}Sr_{0.33}Ca_{0.10})TiO_3$ (BSCT) powders were prepared by a sol-gel method. The BSCT thick films were fabricated by a screen-printing techniques on alumina substrates and then sintered at 1420 °C for 2 h. We also investigated the structural and dielectric properties of BSCT thick films as a function of a variation of Dy_2O_3 content. The results of X-ray diffraction analysis showed a cubic perovskite structure without presence of the second phase in all BSCT thick films. A BSCT thick film doped with 0.1 mol% Dy_2O_3 showed a relatively dense microstructure with an average grain size of 1.26 μm . The thickness of all the BSCT thick films was approximately 60 μm . The Curie temperature of the 0.1 mol% Dy_2O_3 doped BSCT specimens was 0 °C, and the dielectric constant and dielectric loss at this temperature were 6650 and 3.5%, respectively.

Key words: sol-gel, Screen-printing, Thick films, Ferroelectric, Dielectric constant.

Introduction

Perovskite-type barium titanate ($BaTiO_3$) ceramics are the most important electronic materials for use in multilayer ceramic capacitors, positive temperature coefficient (PTC) thermistors, and piezoelectric transducers. More importantly, the electrical conductivity of $BaTiO_3$ ceramics can be controlled by minor modification of the dopants or variation of the sintering conditions without seriously affecting other properties which range from ferroelectricity to semiconductivity. By partially substituting Sr^{2+} and 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 [1, 2]. Ferroelectric $BaTiO_3$ ceramics have recently attracted great interest as membrane sensors, micro-accelerometers and micrometers [3, 4].

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 ceramics [5, 6]. 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. Thick film technology using the screen printing method is most

suitable for the preparation of films of about 10-100 μm thickness. Screen printing method offers simultaneous processing films in the preparation and pattern formation with little material loss. Therefore, it offers high productivity and good cost performance. In this study, $BaTiO_3$ powders, partially substituted with Sr^{2+} and Ca^{2+} ions on the A-site, (Ba^{2+} ions) of the perovskite structure were prepared by a sol-gel method in order to decrease the phase transition temperature to below 0°C and to produce specimens with better dielectric properties at room temperature. Also $(Ba, Sr, Ca)TiO_3$ thick films were fabricated by a screen-printing method. The dependences of the structural and dielectric properties on the Dy_2O_3 content were examined.

Experimental

The chemical composition of the specimens are given according to the following formula: $(Ba_{0.57}Sr_{0.33}Ca_{0.10})TiO_3$ (BSCT) + 0.1 mol% $MnCO_3$ + x mol% Dy_2O_3 (x = 0.1, 0.3, 0.5, 0.7). This BSCT composition gave a transition temperature below room temperature. BSCT powders were prepared by a sol-gel method. Highly pure Ba acetate, Sr acetate and Ca acetate were dissolved in acetic acid (CH_3COOH) and then the solution was heated to evaporate the water. After cooling to 60 °C, 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 800 °C for 2.5 h in a high purity alumina crucible. After this dopants of 0.1 mol% $MnCO_3$ and Dy_2O_3 were added to the calcined powders, these powders were mixed by ball milling for 24 h. The

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screen-printable pastes were prepared by kneading the ground 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 with Pt paste and firing at 1450 °C for 20 minutes. After screen printing, printed films were dried at 80 °C. These processes from printing to drying were repeated six times to obtain the desired thickness. These dried BSCT thick films were uniaxial pressed with 50 MPa and then were sintered at 1420 °C for 2 h with an intermediate 2 h isothermal at 600°C to remove the organic components. The upper electrodes were fabricated by screen printing with Ag paste and then firing at 590 °C for 10 minutes. X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM) were used to investigate the crystallinity and microstructures of thick films, respectively. Also the dielectric properties of the specimens with a variation of temperature and frequency were measured using a LCR-meter and electrometer.

Results and Discussion

Fig. 1 shows the differential thermal analysis (DTA) and the thermogravimetry (TG) curves of the dried BSCT (57/33/10) powders. The weight loss of dried powders derived from the sol-gel method was about 37% at 1000 °C, as determined by the TG curve. An endothermic peak 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 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 [6]. The exothermic peak was observed at around 660 °C due to the formation of the polycrystalline perovskite phase.

Fig. 2 shows the X-ray diffraction patterns (XRD) of the Dy₂O₃ doped BSCT(57/33/10) thick films. All the BSCT thick films showed the formation of a complete solid solution in a cubic polycrystalline structure without

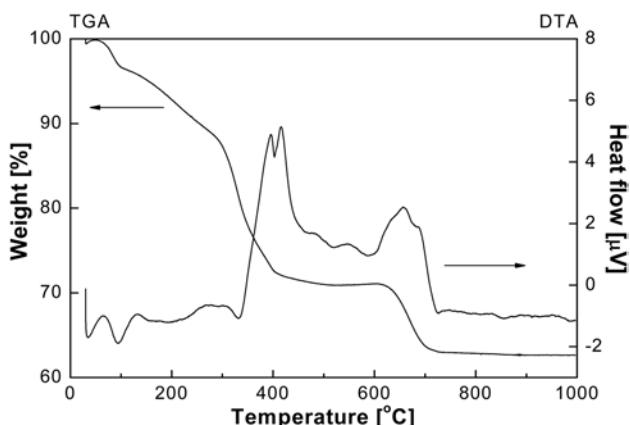


Fig. 1. DTA/TGA curves of the dried BSCT (57/33/10) powders.

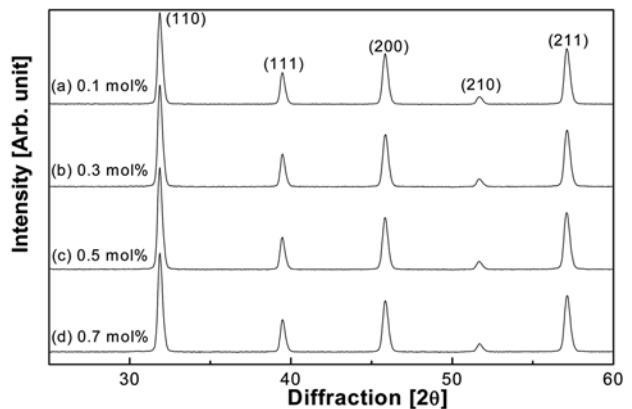


Fig. 2. XRD patterns of BSCT (57/33/10) specimens with various Dy₂O₃ contents.

a preferred orientation; no pyrochlore phase was observed. The lattice constant, calculated from the XRD patterns, of the BSCT thick films decreased with an increase the Dy₂O₃ content because the radius of the Dy³⁺ ion (0.099 nm) is smaller than that of the Ba²⁺ ion (0.135 nm). The values of the lattice constants for the BSCT thick film doped with 0.1 mol% and 0.7 mol% Dy₂O₃ are 0.3945 nm and 0.3931 nm, respectively.

Fig. 3 and 4 show the surface and cross sectional SEM micrographs of BSCT thick films with variation of Dy₂O₃ content. The BSCT thick film doped with 0.1 mol% Dy₂O₃ showed a relatively dense microstructure with an average grain size of 1.26 μm. However, the grain size decreased with an increase in amount of Dy₂O₃ amount, the BSCT thick film doped with 0.7 mol% Dy₂O₃ exhibited a porous microstructure with a grain size of 0.85 μm. This is due to the fact that Dy³⁺ ions act as the donor dopants in the BSCT specimens [7]. The thickness of all the BSCT thick films was approximately 60 μm.

Fig. 5 and 6 shows the relative dielectric constant and dielectric loss of BSCT thick films as a function of temperature for various Dy₂O₃ contents at 1 kHz. The Curie temperature of the 0.1 mol% Dy₂O₃ doped BSCT specimen was 0 °C, and the dielectric constant and dielectric loss at this temperature were 6650 and 3.5%, respectively. The addition of Dy₂O₃ to BSCT specimens caused a decrease in the Curie temperature and the maximum dielectric constant, because it created cation vacancies in the lattice which are used to maintain electroneutrality [8]. The dielectric loss properties were independent of the amount of Dy₂O₃ and all specimens showed good values of less than 1% at above room temperature.

Conclusions

BSCT(57/33/10) powders were prepared by the sol-gel method, and BSCT thick films doped with Dy₂O₃ were fabricated on alumina substrates using a screen printing technique. Structural and dielectric properties were

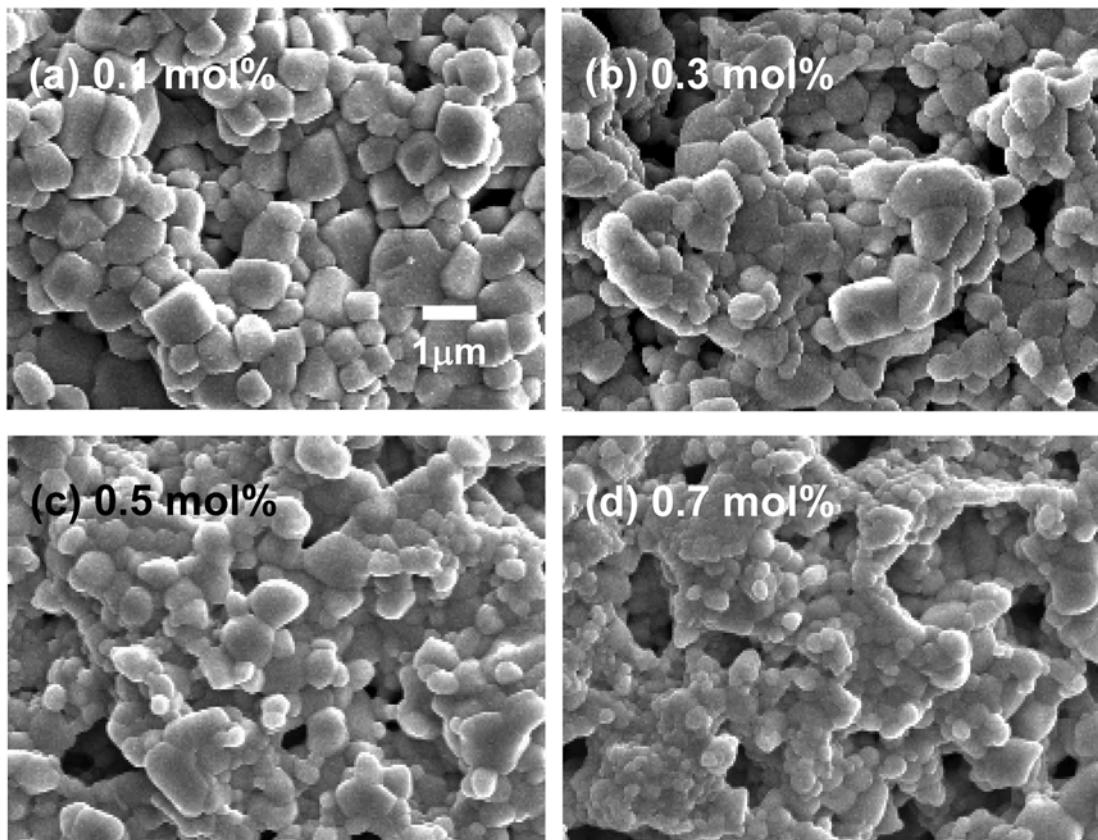


Fig. 3. Surface SEM micrographs of BSCT (57/33/10) specimens with various Dy_2O_3 contents.

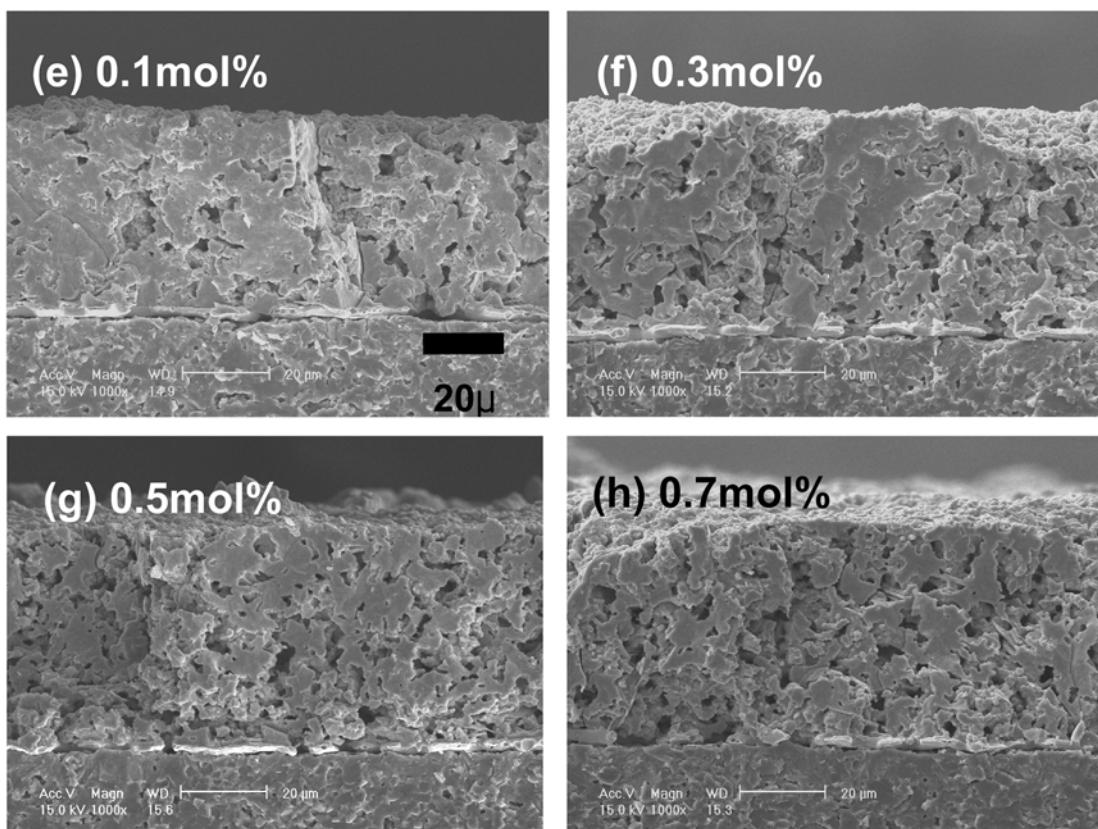


Fig. 4. cross-sectional SEM micrographs of BSCT (57/33/10) specimens with various Dy_2O_3 contents.

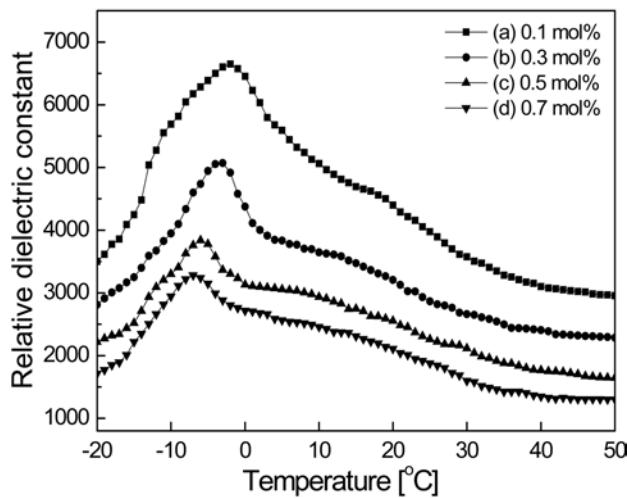


Fig. 5. Relative dielectric constant of BSCT (57/33/10) thick films as a function of temperature and Dy₂O₃ contents at 1 kHz.

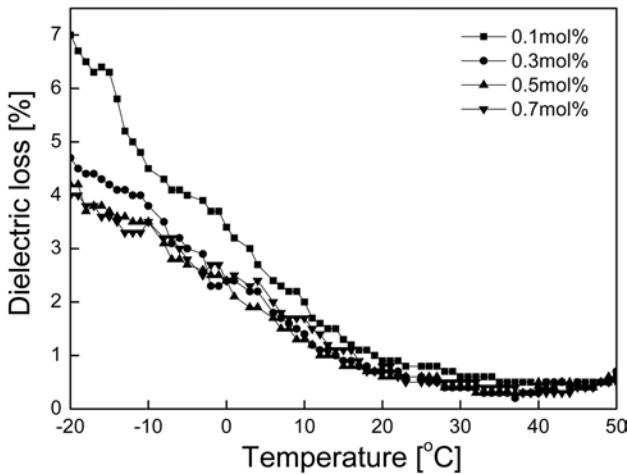


Fig. 6. Dielectric loss of BSCT (57/33/10) thick films as a function of temperature and Dy₂O₃ contents at 1 kHz.

investigated for various amount of Dy₂O₃. An exothermic peak was observed at around 660 °C due to the formation of the polycrystalline perovskite BSCT phase. The lattice constant and grain size of the BSCT thick films decreased with an increase in the Dy₂O₃ content, and these values for the BSCT thick film doped with 0.7 mol% Dy₂O₃ is 0.3931 nm and 0.85 mm, respectively. The addition of Dy₂O₃ to BSCT specimens caused a decrease in the Curie temperature and the maximum dielectric constant, because it created cation vacancies in the lattice which are used to maintain of electroneutrality.

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