Dielectric and Pyroelectric Properties of Dy-doped BSCT Thick Films by Screen-printing Method

Hyun-Ji Noh*, Sung-Gap Lee† and Sung-Pill Nam*

Abstract – $(Ba_{0.57}Sr_{0.33}Ca_{0.10})TiO_3$ (=BSCT) powders, prepared by the sol-gel method, were doped using $MnCO_3$ as the acceptor and Dy_2O_3 as the donor. This powder was mixed with an organic vehicle. BSCT thick films were fabricated by the screen-printing techniques on the alumina substrate. The structural and dielectric properties of BSCT thick films were investigated with variation of the Dy_2O_3 amount. As a result of the differential thermal analysis (DTA), the exothermic peak was observed at around 670°C due to the formation of the polycrystalline perovskite phase. All the BSCT thick films showed the XRD patterns of a typical polycrystalline perovskite structure. The average grain size of BSCT thick films decreased with an increasing amount of Dy_2O_3. The relative dielectric constant and dielectric loss of the BSCT thick film doped Dy_2O_3 0.1mol% were 4637.4 and 1.6% at 1kHz, respectively.

Keywords: Ferroelectric, Dielectric constant, Thick film, Screen-printing

1. Introduction

Perovskite substances with an ABO_3 structure are known as general materials used for the applications of electronic ceramic devices [1]. Due to their unique properties, perovskite ferroelectric materials are very attractive for applications to capacitors of dynamic random access memories (DRAMs), piezo micro actuators, pyroelectric infrared detectors, and non-linear optical devices [2-4]. Among the various ferroelectrics, $BaTiO_3$ materials have been intensively investigated due to their high spontaneous polarization and high dielectric constant properties. $BaTiO_3$ could have good electric properties by modifying the dopant and controlling variation conditions. Recently, using these great properties as an application for multilayer ceramic capacitors, positive temperature coefficient (PTC) thermistors, piezoelectric transducers, dynamic random access memorials, uncooled infrared detector materials and tunable oscillators [5-7]. It is well known, however, that the ferroelectric properties of $BaTiO_3$ deteriorate with decreasing film thickness compared to those of bulk ceramics. When the film thickness of $BaTiO_3$ is less than 1m, the dielectric constant and the remanent polarization decrease due to surface stress.

In this study, $BaTiO_3$ powders, partially substituted with Sr^{+2} and Ca^{+2} ion at the A-sites (Ba^{+2} ions), were prepared using the sol-gel method in order to decrease to the phase transition temperature down to below 0℃ and to improve the dielectric properties. It is possible that it affected the structural and electric properties with the addition of minor dopant in BSCT ceramics [8], [9]. And the $(Ba_{0.57}Sr_{0.33}Ca_{0.10})TiO_3$ doped Dy_2O_3 thick films were fabricated using the screen printing method and the structural and dielectric properties with a varying amount of Dy_2O_3 were investigated.

2. Experimental

The chemical compositions of the specimens are given according to the following formula: $(Ba_{0.57}Sr_{0.33}Ca_{0.10})TiO_3$ + 0.1 mol% $MnCO_3$ + x mol% Dy_2O_3 (x=0.1, 0.3, 0.5, 0.7). These BSCT compositions gave a transition temperature below room temperature. BSCT powders were prepared using the sol-gel method. Highly pure Ba acetate, Sr acetate and Ca acetate was dissolved in acetic acid (CH_3COOH) and the solution was then heated for the evaporation of 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 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 dopant of 0.1mol% $MnCO_3$ and Dy_2O_3 were added to the calcined powders, these powders were mixed by ball milling for 24 h. The screen-printable pastes were prepared by kneading in the ground powder with 30wt% 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 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 six times to obtain the desired thickness. These dried BSCT

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thick films were uniaxial pressed with 0.5 ton/cm^2 and were then sintered at 1420°C for 2 h in the close 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.

The differential thermal analysis (DTA) and the thermogravimetry analysis (TGA) curves, X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM) were used to investigate the structural properties. The dielectric properties were measured using a LCR-meter (Fluke, PM6306) with variation temperature (Delta Design, Delta 9023) and frequency.

3. Results and Discussion

Fig. 1 Shows the differential thermal analysis (DTA) and the thermogravimetry (TGA) curves of the dried $(Ba_{0.57}Sr_{0.33}Ca_{0.10})TiO_3$ powders. The exothermic peaks were observed in the temperature range of 340~450°C due to the combustion of organic residues and the weight loss was about 27%. The exothermic peaks observed around 670°C was attributed to finish the decomposition of $(Ba_{0.57}Sr_{0.33}Ca_{0.10})TiO_3$ powder which formed during heating [9].

The weight loss of the dried powders derived from the sol-gel method was 37% at 1000°C, as determined by the TG curve. According to this result, the $(Ba_{0.57}Sr_{0.33}Ca_{0.10})TiO_3$ powder was calcined at 800°C and the tempereture was estimated at the formation of the polycrystalline perovskite phase.

Fig. 2 Shows the X-ray diffraction patterns (XRD) of the Dy_2O_3 doped $(Ba_{0.57}Sr_{0.33}Ca_{0.10})TiO_3$ thick films printed on the alumina substrate. All the BSCT thick films showed the typical XRD patterns of a perovskite polycrystalline structure without a secondary phase. This suggests that the sintering conditions of BSCT thick films were adequate and Dy_2O_3 was deposited at the BSCT structure. In the XRD pattern, (111) the peak shifted the high angle with an increased amount of Dy_2O_3 and a difference is seen in structual and electrical properties.

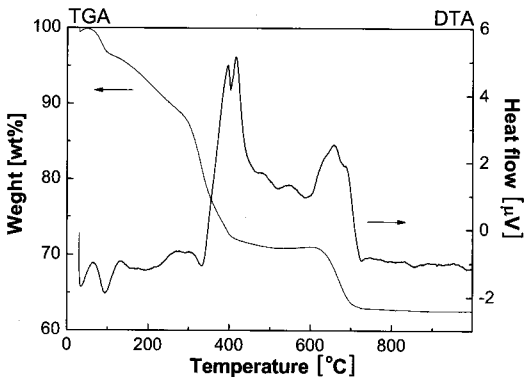

Fig. 1. TGA/DTA curves of the $(Ba_{0.57}Sr_{0.33}Ca_{0.10})TiO_3$ powders.

Fig. 3 shows the surface and cross-sectional FE-SEM micrographs of the $(Ba_{0.57}Sr_{0.33}Ca_{0.10})TiO_3$ thick films for various Dy_2O_3 contents. All thick films exhibited uniform grain structure. The grain size decreased with an increased amount of Dy_2O_3 because a portion of the doping Dy ions precipitate out of the normal grains and remain at the grain boundaries which subsequently resist the grain growth. The average thickness of all BSCT thick films was about 60 μm and the average grain size with 0.1 mol% Dy_2O_3 doped thick films was about 1 μm.

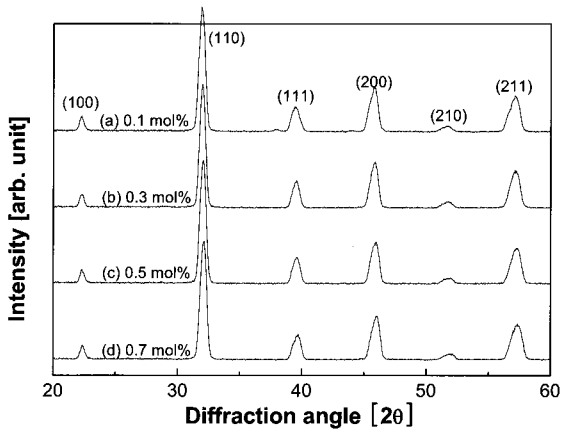

Fig. 2. XRD patterns of $(Ba_{0.57}Sr_{0.33}Ca_{0.10})TiO_3$ specimens with various Dy_2O_3 contents.

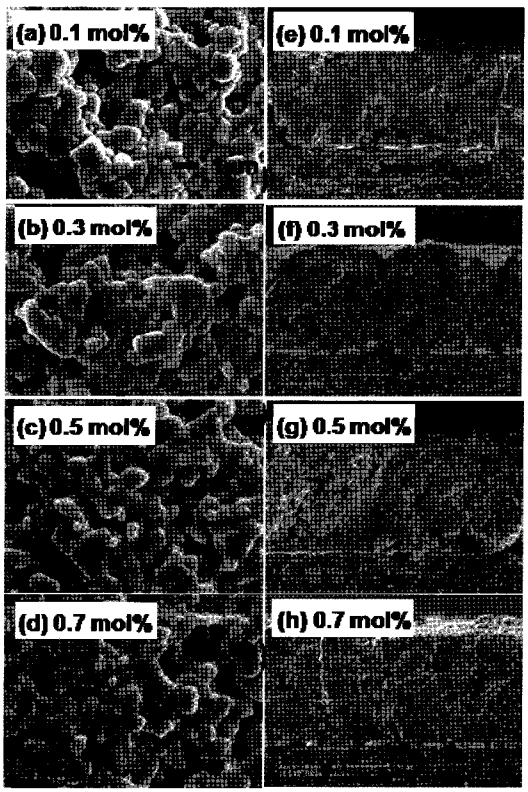

Fig. 3. Surface and cross-sectional FE-SEM micrographs of $(Ba_{0.57}Sr_{0.33}Ca_{0.10})TiO_3$ specimens with various Dy_2O_3 contents.

Figs. 4 and 5 show the variation of relative dielectric

constant and the dielectric loss at 1 kHz of BSCT thick films as a function of temperature for various Dy_2O_3 contents, respectively. The relative dielectric constant and the Curie temperature of BSCT thick films decreased with an increase in the Dy_2O_3 amount due to the effect of decreasing the grain size. The Dy ions were deposited at grain boundaries, inhibit grain growth and it was effected properties [11].

These properties may be understood in terms of the effects of the decreasing grain size and the creation of cation vacancies. When donor ions with a higher valence replace metal ions with a lower positive valence in the ABO_3 perovskite structure, cation vacancies are created in the lattice, an account of the requirements of electroneutrality.

These cation vacancies cause shrinkage of the lattice and affect the transition temperature. The dielectric loss of the BSCT thick films decreased with an increase in the amount of Dy_2O_3. However, the values of all specimens were less than 1.0 % at around room temperature.

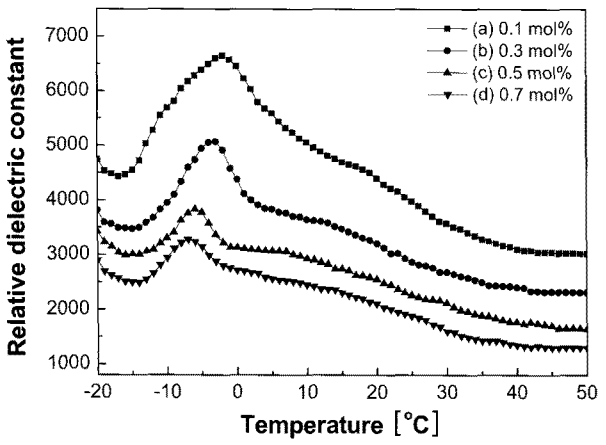

Fig. 4. Relative dielectric constant as a function of temperature for $(Ba_{0.57}Sr_{0.33}Ca_{0.10})TiO_3$ thick films with various Dy_2O_3 contents.

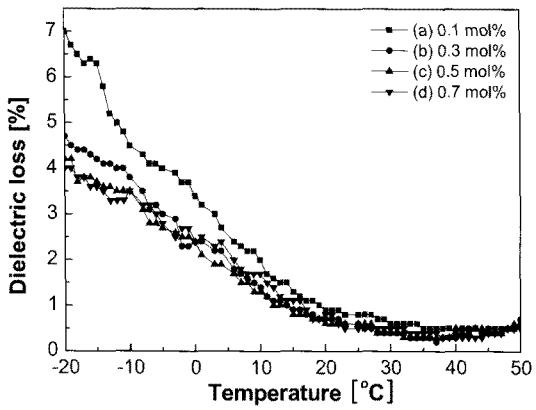

Fig. 5. Dielectric loss as a function of temperature for $(Ba_{0.57}Sr_{0.33}Ca_{0.10})TiO_3$ thick films with various Dy_2O_3 contents.

Figs. 6 and 7 shows the pyroelectric properties of BSCT thick films with the variation of temperature and Dy_2O_3 contents. The pyroelectric coefficient showed the dielectric constant-temperature curve, and 0.1 mol% Dy_2O_3 doped BSCT thick films indicated 21.5×10^{-9} [C/cm^{2}K] pyroelectric coefficient at 0°C.

The figure of merit F.M.D* was derived from:

$$F.M.D^*=p/[c_v\times(\tan\ )]^{1/2}$$

where p is the pyroelectric coefficient, c_v(=3.2J/cm$_3$K) is volume specific heat, . is relative permittivity and tan . is the dielectric loss[12]. F.M.D* is has useful parameters for pyroelectric materials and to judge the suitability of new materials for applications in pyroelectric infrared detectors. The F.M.D* of 0.7 mol% Dy_2O_3 doped BSCT thick films indicated 1.9×10^{-9} [C/cm^{2}J] at -2°C.

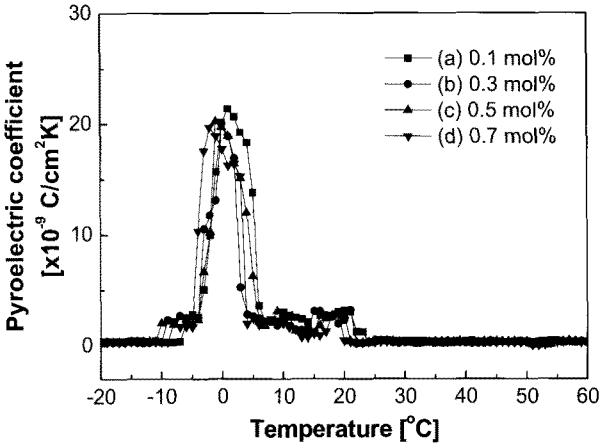

Fig. 6. Pyroelectric coefficient of $(Ba_{0.57}Sr_{0.33}Ca_{0.10})$ TiO_3 thick films as a function of temperature.

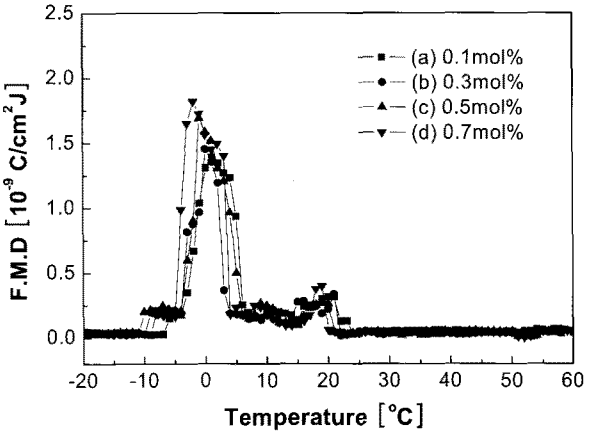

Fig. 7. Fiture of merit F.M.D* of $(Ba_{0.57}Sr_{0.33}Ca_{0.10})TiO_3$ thick films as a function of temperature.

4. Conclusion

$(Ba_{0.57}Sr_{0.33}Ca_{0.10})TiO_3$ powder doped with $MnCO_3$ and Dy_2O_3 were prepared using the sol-gel method and the BSCT thick films were fabricated using the screen printing method on high purity alumina substrate. The structure and

electric properties were investigated with a variation of Dy_2O_3 contents. All BSCT thick films exhibited a cubic perovskite structure without a second phase. The variation of Dy_2O_3 contents influenced the microstructure and the Curie temperature. The lattice constant and grain size decreased with increased amounts of Dy_2O_3. The average thickness of all BSCT thick films was about 60 μm. The Curie temperature of doped 0.1 mol% Dy_2O_3 BSCT thick films was -2°C. The relative dielectric constant and the Curie temperature of BSCT thick films decreased with increased amounts of Dy_2O_3 due to the effect of decreasing the grain size. The grain size of BSCT thick films doped with 0.1 mol% Dy_2O_3 content was about 1μm, and showed the highest relative dielectric constant of 4637.4 at room temperature.

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