Microwave Dielectric Properties of BSCT Thick Films with Addition of Nb_2O_5

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Abstract

$(Ba,Sr,Ca)TiO_3$ powders, prepared by the sol-gel method, were mixed with organic vehicle and the BSCT thick films were fabricated by the screen printing techniques on alumina substrates. The dielectric properties were investigated for various composition ratio and Nb_2O_5 doping contents. All the BSCT thick films, sintered at 1420℃, showed the typical XRD patterns of a perovskite polycrystalline structure. The Curie temperature and the relative dielectric constant decreased with increasing Ca content and Nb_2O_5 doping amount. The relative dielectric constant, dielectric loss and tunability of the BSCT(50/40/10) thick films doped with 1.0wt% Nb_2O_5 were 1410, 0.65% and 17.29% respectively.

Key Words : BSCT ceramics, Screen-Printing method, Thick films, Dielectric properties

1. Introduction

The microwave phase shifter is an essential element in many different communication and radar systems. As an example, each radiating element of a phased array antenna must have an independent phase shifter in order to electronically steer the radiated beam. Tuning of the microwave devices can be achieved by ferroelectric ceramics [1]. The desired characteristics of the dielectric material of choice for phase array applications should be; moderate to low dielectric constant at microwave frequencies, low dielectric loss and a large variation of the dielectric constant with applied DC biasing field [2]. Several materials have been proposed for such application. However, the high inherent material loss and high dielectric constant of $BaTiO_3$ system bulk ceramics have restricted its application in phased array antennas.

On the other hand, thin or thick films of high dielectric constant ferroelectrics are interesting for planar integrated microwave circuits. But, surface stress in very thin films ($<1\mu m$) results in a significant decrease of the dielectric constant and the tunability, and an increase of the dielectric loss compared to bulk $BaTiO_3$ system ceramics. Ferroelectric thick film materials possess merits of bulk materials and thin films.

In this study, $BaTiO_3$ powders, partially substituted with Sr^{+2} and Ca^{+2} ions at the A-sites (Ba^{+2} ions) and Nb^{+5} ions at the B-sites (Ti^{+4} ions), were prepared by the sol-gel method in order to decrease the phase transition temperature down to below 0℃ and to produce specimens with better dielectric properties for application in microwave phase shifters. $(Ba,Sr,Ca)TiO_3$ thick films were fabricated by a screen printing method on alumina substrates. The structural and dielectric properties on the composition ratio and the Nb_2O_5 content were examined.

2. Experimental

The chemical compositions of the specimens are given by the formula $(Ba_{0.6-x}Sr_{0.4}Ca_x)TiO_3$ (BSCT) + ywt% Nb_2O_5 (x=0.10, 0.15, 0.20,

y=0~3.0). BSCT powders, started with mixture of Ba acetate, Sr acetate hemihydrate, Ca acetate monohydrate and Ti isopropoxide were prepared by the sol-gel method. Acetic acid and 2-methoxyethanol were used as solvents. Ba, Sr and Ca acetate were dissolved in acetic acid, and then the solution was heated to evaporate of water. After cooling, 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 in a high purity alumina crucible. After dopant of Nb_2O_5 was added to the calcined powders, these powders were mixed and ground by planetary ball milling. The ground powder had a particle size ranging from 0.35 to 0.8mm with the mean diameter of 0.53mm.

The screen-printable pastes were prepared by kneading the ground BSCT powder with organic vehicle (Ferro. B75001). High purity alumina was used as a substrate. The bottom electrodes were prepared by screen printing Pt paste and firing at 1450℃ for 20min. After screen printing the BSCT paste, printed films were dried and these processes from printing to drying were repeated four times to obtain a desired thickness. The thick films were sintered at 1420℃ for 2h in the closed alumina crucible. The upper electrodes were fabricated by screen printing the Ag paste and then firing at 850℃ for 30min.

X-ray diffraction was introduced in order to analyze the crystallinity of BSCT specimen. The dielectric properties were measured using on impedance material analyzer (HP 4294). The % tunability was determined using the following equation; % tunability = $\{K(0)-K(V_{appl.})\} / K(0)$, where K(0) is the relative dielectric constant without DC bias and $K(V_{appl.})$ is the relative dielectric constant with $V_{appl.}$ The tunability measurements were taken as a function of applied electric field, with ranged from 0 to 30 kV/cm.

3. Results and discussion

Figure 1 shows the X-ray diffraction patterns of the Nb_2O_5-doped BSCT(40/40/20) thick films sintered at 1420℃. All the BSCT thick films showed the typical XRD patterns of a perovskite polycrystalline structure without a preferred orientation: no pyrochlore phase was observed.

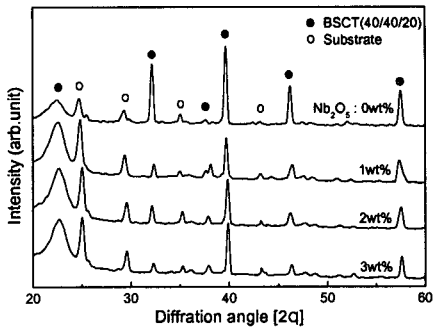

Fig. 1. X-ray diffraction patterns of the Nb_2O_5-doped BSCT(40/40/20) thick films sintered at 1420℃.

Figure 2 shows the relative dielectric constant at 1MHz of BSCT thick films as a function of temperature for various Nb_2O_5 contents. The Curie temperature of BSCT specimens decreased with decreasing Ba/(Sr+Ca) ratio. For substitution Sr^{2+}-Ba^{2+}, the bonding force between the A-site ion and the oxygen of ABO_3 perovskite structure becomes stronger because the radius of the Ba^{2+} ion (0.135nm) is larger than that of the Sr^{2+} ion (0.113nm): the bonding force Ti-O(Sr), therefore, becomes weaker than the Ti-O(Ba) 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 [3]. Nb ions, act on the donor dopant, cause the creation of more space charges in BSCT specimens, the BSCT(50/40/10) thick film doped with 1wt% Nb_2O_5 showed the high dielectric constant of 1410. However, the dielectric constant of the BSCT specimens with more than 2wt% Nb_2O_5 decreased due to

decreasing the grain size and increasing the lattice distortion of unit cell with an excessive doping.

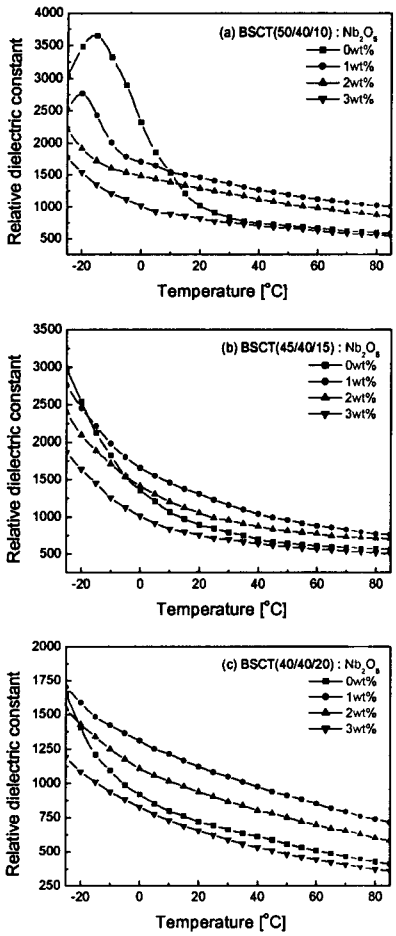

Fig. 2. Relative dielectric constant as a function of temperature for BSCT thick films with various Nb_2O_5 contents.

Figure 3 shows the variation of the relative dielectric constant of BSCT thick films as a function of frequency for various Nb_2O_5 contents. The relative dielectric constant decreases in the measured frequency range from 0.5GHz to 1GHz and gradually saturates at around 1GHz. This suggests that the relaxation frequency of the dipolar polarization is about 0.7GHz for all specimens.

Figure 4 shows the tunability of BSCT thick films as a function of Nb_2O_5 content at 1MHz. The tunability is defined as the percentage

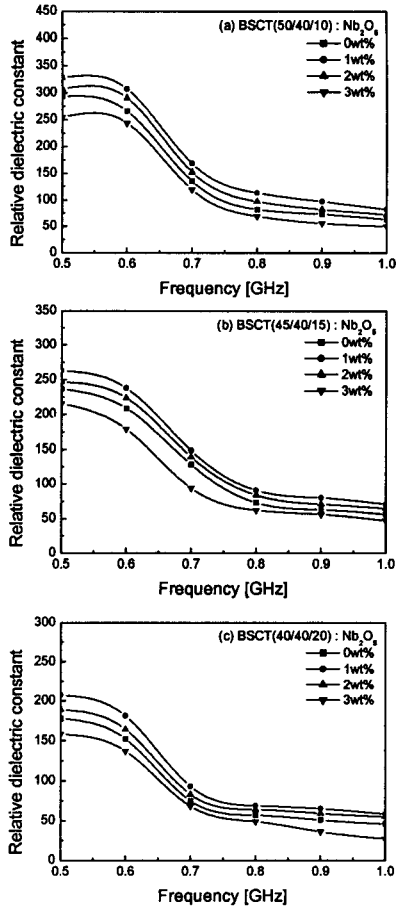

Fig. 3. Relative dielectric constant as a function of frequency for BSCT thick films with various Nb_2O_5 contents.

change of the relative dielectric constant at 30kV/cm. The tunability of the BSCT thick films increased with decreasing Ca contents because the displacement of ions was strongly influenced by the external fields at around the Curie temperature. When donor dopants are doped for cation ions in the ABO_3 perovskite structure, A-site vacancies are created in the lattice to satisfy charge neutrality. Dipoles

formed from donor substitutes and barium vacancies were easier oriented by an applied field [4]. Therefore, the BSCT(50/40/10) thick film doped with 1.0wt% Nb_2O_5 showed the highest tunability of 17.29%. However, the tunability of the specimens doped with more than 2.0wt% Nb_2O_5 decrease due to increasing the distortion of the unit cell with an excessive doping and the increasing internal stress with decreasing grain size.

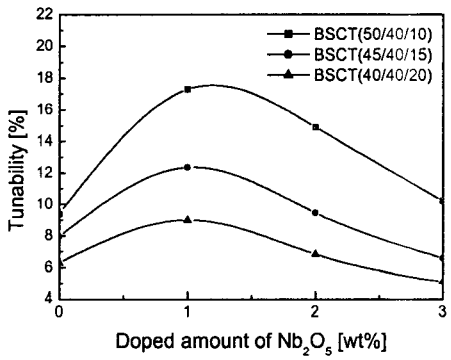

Fig. 4. Tunability of BSCT thick films with various Nb_2O_5 content at 1MHz.

4. Conclusions

$(Ba,Sr,Ca)TiO_3$ powders doped with Nb_2O_5 were prepared by sol-gel method and the BSCT thick films were fabricated by the screen printing techniques on alumina substrates. All BSCT thick films showed a perovskite polycrystalline structure without a pyrochlore phase. The Curie temperature of BSCT specimens decreased with decreasing Ba/(Sr+Ca) ratio. The relative dielectric constant and Curie temperature of BSCT thick films decreased with increasing Nb_2O_5 amount. The relative dielectric constant decreases with increasing the applied DC field because the applied electric fields acts on the non-ferroelectric grains in such a way as to induce a ferroelectric state in those grains. The tunability of the BSCT specimens was affected by the phase transition temperature and microstructures such as grain size.

Acknowledgements

This work was supported by Korea Research Foundation Grant (KRF-2001-042-E00042).

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