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# Dielectric properties of $Yb_2O_3$-doped barium strontium calcium titanate thick films for microwave device applications

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**Abstract** $(Ba_{0.56}Sr_{0.34}Ca_{0.10})TiO_3$ (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 substrate. The structural and electrical properties as a function of $Yb_2O_3$ amount were investigated. All BSCT thick films showed the formation of a complete solid solution in a cubic perovskite polycrystalline structure. Average grain size of the specimen doped with 0.7 mol% $Yb_2O_3$ was about 2.7 μm. The thickness of all BSCT thick films was approximately 50–55 μm. The relative dielectric constant, dielectric loss, and tunability of the BSCT thick films doped with 0.3 mol% $Yb_2O_3$ were 2,966, 0.7, and 14.3%, respectively.

## Introduction

Perovskite-type barium titanate ($BaTiO_3$) ceramics is one of the most important electronic materials for use in dielectric materials, 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 sintering conditions without seriously affecting other properties that range from ferroelectricity to semiconductivity. By partially substituting $Sr^{2+}$ 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 [1].

$BaTiO_3$-system ceramics are being investigated with considerable interest as new dielectric materials for future-generation dynamic random access memories (DRAMs) and more recently for tunable microwave application. The large electrical field-dependent dielectric constant can be used for tunable microwave devices, such as tunable oscillators, phase shifters, and varactors [2]. The optimal electronic parameters for the dielectric material of choice for phase array applications should be a moderate-to-low dielectric constant ($30 < K < 1,000$), a low dielectric loss ($\tan\delta < 0.01$), and a large tunability [3]. 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, ferroelectric thick film materials possess the merits of bulk materials and thin films. Devices made from thick films not only work at low voltage and high frequency and are compatible with semiconductor integrated circuits but also possess superior electric properties, approaching close to the bulk values.

In this study, ferroelectric $BaTiO_3$ powders, partially substituted with $Sr^{+2}$ and $Ca^{+2}$ ions at the A-sites ($Ba^{+2}$ ions) were prepared by a sol–gel method in order to decrease the phase transition temperature and to improve the dielectric properties at near the room temperature. $(Ba,Sr,Ca)TiO_3$ thick films were fabricated by the screen-printing method on alumina substrates. For perovskite structure, doping with small amounts of donor dopant can greatly affect the dielectric properties, and the Yb ion can act as donor dopant. The structural and dielectric properties were investigated for microwave devices applications.

## Experimental

The chemical compositions of the samples are given by the formula: $(Ba_{0.54}Sr_{0.36}Ca_{0.1})TiO_3$ + 0.1 mol% $MnCO_3$ +

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y mol% $Yb_2O_3$ ($y = 0.1$, 0.3, 0.5, 0.7). These BSCT compositions gave a transition temperature below room temperature. Doped BSCT specimens with 0.1 mol% $MnCO_3$ were selected for their basic composition on the basis of previous experiments [4]. BSCT powders, started with a mixture of Ba acetate ($Ba(CH_3COO)_2$), Sr acetate ($Sr(CH_3COO)_2(0.5H_2O)$, Ca acetate ($Ca(CH_3COO)_2(H_2O)$, 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. The calcined BSCT powders, doped with $Yb_2O_3$ and $MnCO_3$, were mixed and ground by planetary ball milling for 24 h.

The screen-printable pastes were prepared by kneading the ground BSCT powder in a non-bubbling kneader (NBK-1, Kyoto Electro.) with 30 wt% of organic binder which consisted of ethyl cellulose and α-terpineol. High purity alumina was used as a substrate. The bottom electrodes were prepared by screen-printing method Pt paste and firing at 1,450°C for 2 h. Screen-printed layers were printed onto alumina substrates using a screen-printing machine (Model HSP-12A, Hansung, Korea). After the BSCT paste had been screen printed using a 200-mesh screen mask, printed films were allowed to level for 10 min and were then dried at 400 °C for 20 min. These processes from printing to drying were repeated 4-times to obtain the desired thickness. The thick films were sintered at 1,420 °C for 2 h in air with an intermediate 2 h isothermal at 600 °C to remove the organic components. The upper electrodes were fabricated by screen-printing Ag paste and then firing at 850 °C for 30 min. Figure 1 shows a flow chart for the BSCT thick films preparation process.

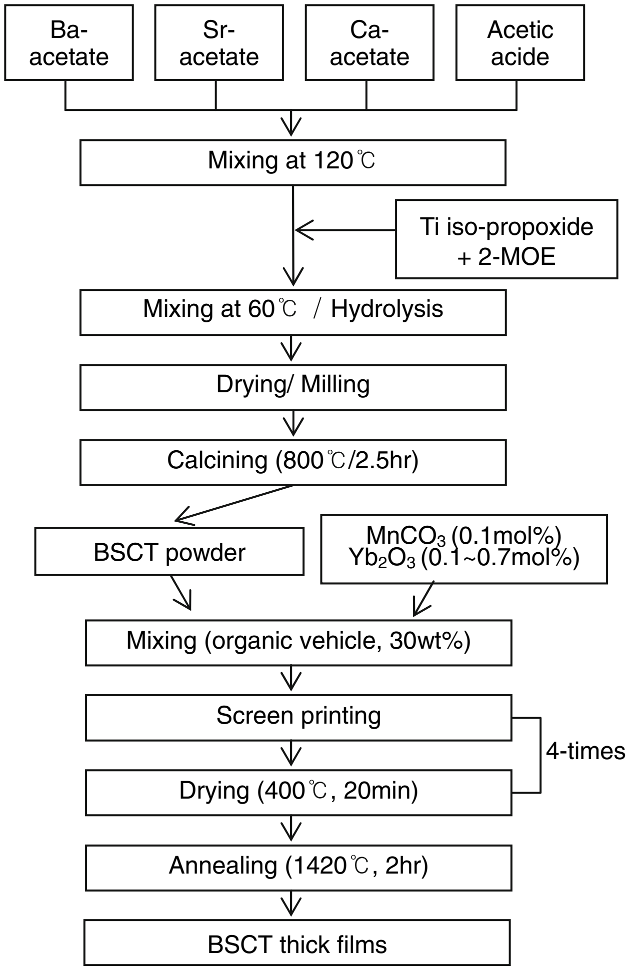

**Fig. 1** Flow chart of BSCT powder preparation

X-ray diffraction (XRD) and scanning electron microscopy (SEM) were introduced in order to analyze the crystallinity and the microstructure of BSCT specimens, respectively. The dielectric properties of the specimens were measured using an impedance analyzer (HP 4194). The tunability was determined using the following equation [5]:

$$\%\ \text{tunability} = \{K(0) - K(V_{\text{appl}})\}/K(0) \tag{1}$$

where $K(0)$ is the relative dielectric constant without dc bias and $K(V_{\text{appl}})$ is the relative dielectric constant with $V_{\text{appl}}$. The tunability measurements were taken as a function of the applied voltage, which ranged from 0 to 40 V.

## Results and discussions

Figure 2 shows the differential thermal analysis (DTA) and the thermogravimetry (TG) curves of the dried BSCT(54/36/10) powders. The weight loss of dried powders derived from the sol–gel method was about 42% at 1,000 °C, as determined by the TGA curve. An endothermic peak due to the evaporation of absorbed water and solvent were observed in the temperature range of 100–350 °C. Due to the decomposition of acetate, exothermic peaks were observed at around 400 °C [6]. The weight loss in the temperature range of 600–700 °C was attributed to the

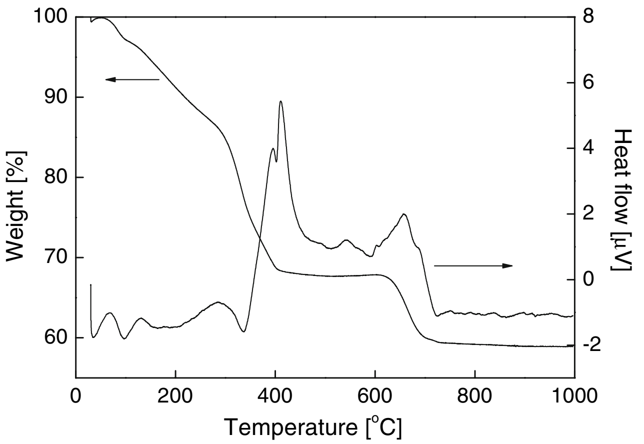

**Fig. 2** DTA/TGA curves of the dried BSCT(54/36/10) powder

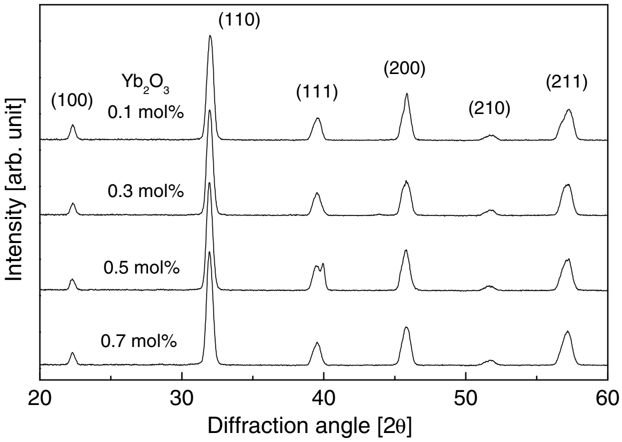

**Fig. 3** XRD patterns of the BSCT thick films as a function of $Yb_2O_3$ amount

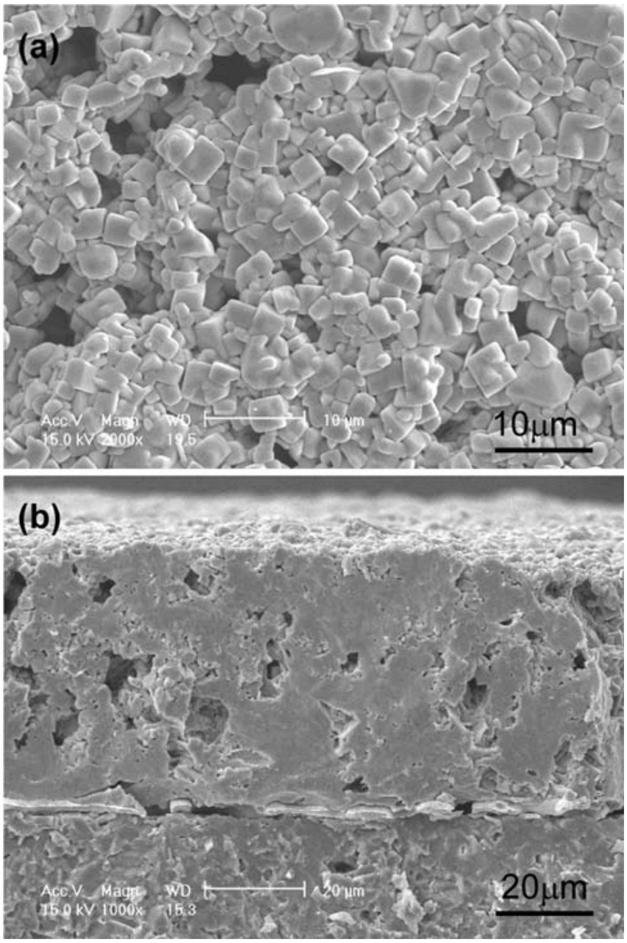

**Fig. 4** Surface and cross-sectional SEM micrographs of the BSCT thick films doped with 0.7 mol% $Yb_2O_3$

decomposition of barium carbonate, which was formed during heating [7]. The exothermic peak was observed at around 660 °C due to the formation of the polycrystalline perovskite phase.

Figure 3 shows XRD patterns of the $Yb_2O_3$-doped BSCT thick films sintered at 1,420 °C. All BSCT thick films showed the formation of a complete solid solution in a cubic perovskite polycrystalline structure. The lattice constants, calculated from the XRD patterns, of BSCT specimens decreased with increasing $Yb_2O_3$ contents because the radius of the $Yb^{3+}$ ion (0.094 nm) is smaller than those of the $Ba^{2+}$ (0.135 nm), $Sr^{2+}$ (0.113 nm), and $Cr^{2+}$ (0.099 nm). The values of the lattice constants for the BSCT thick film doped with 0.1, 0.3, 0.5, and 0.7 mol% $Yb_2O_3$ are 0.3944, 0.3940, 0.3939, and 0.3938 nm, respectively.

Figure 4 shows the surface and cross-sectional SEM micrographs of the BSCT-0.7 mol% $Yb_2O_3$ thick films, which were sintered at 1,420 °C for 2 h. All the BSCT specimens exhibited a relatively dense and uniform grain structure. Average grain size of the specimen doped with 0.7 mol% $Yb_2O_3$ was about 2.7 μm and there is no dependence on the variation of the $Yb_2O_3$ contents. The thickness of the BSCT thick films was determined from SEM observation of cross-sectional fracture surfaces. Five specimens for each $Yb_2O_3$ contents were measured, and the thickness of all the specimens was approximately 50–55 μm.

Figure 5 shows relative dielectric constant and dielectric loss of BSCT thick films as a function of $Yb_2O_3$ at 1 kHz. When donor ions with a higher positive valence replace metal ions with a lower positive valence in the $ABO_3$ perovskite structure, A-site vacancies are created in the lattice to maintain the electroneutrality. Generally, in the $BaTiO_3$ system, A-site vacancies are far less mobile than oxygen vacancies. $O^{2-}$ ions form a continuous network so that vacancies can move by a simple exchange with an adjacent $O^{2-}$ ion. $Ba^{2+}$ ions not so readily exchange sites with them. Thus, dipoles form from donor substitutes and barium vacancies will be stable; they will be slow to form and to orientate [8]. Therefore, because Yb ions act on the donor dopant and cause the creation of more space charges in BSCT specimens, the BSCT thick films doped with 0.3 mol% $Yb_2O_3$ showed the high dielectric constant of 2,970 at 25 °C. However, the dielectric constant of the BSCT specimens with more than 0.5 mol% $Yb_2O_3$ decreased due to the increasing lattice distortion of the unit cell with excess doping. The dielectric loss properties were independent of the $Yb_2O_3$ amount and were less than 0.01 at room temperature. This small value is enough for applications to various electronic devices.

Figure 6 shows the applied DC voltage dependence of the relative dielectric constant for BSCT thick films at 1 MHz. The relative dielectric constant of all specimens decreased with increasing the applied DC voltage. This is because the applied voltages suppress the displacement of ions inside the grains of paraelectric phase. Also, the non-linear dependence

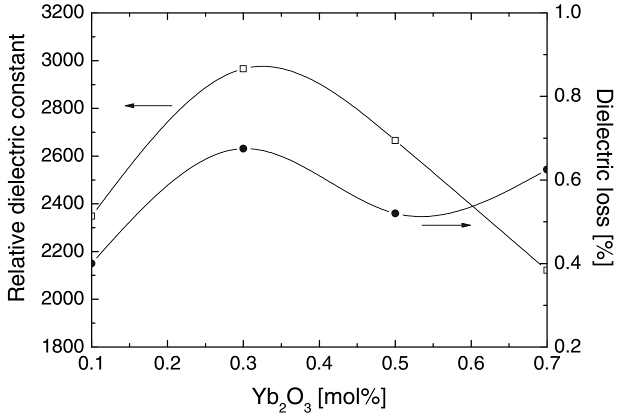

**Fig. 5** Relative dielectric constant and dielectric loss of BSCT thick films as a function of $Yb_2O_3$ amount

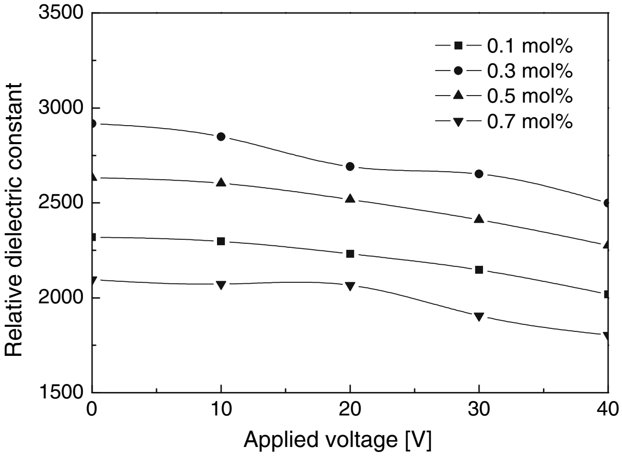

**Fig. 6** Relative dielectric constant as a function of the dc voltage for BSCT thick films with various $Yb_2O_3$ contents

of dielectric constant on the applied DC voltage results from the chemical inhomogeneities in polycrystalline specimens and/or existence of interfacial layers between the metal electrode and the thick films [9].

Figure 7 shows the tunability of BSCT thick films as a function of $Yb_2O_3$ content at 1 MHz. The tunability is defined as the percentage change of the relative dielectric constant at 40 V. Generally, the tendencies of the tunable characteristics in the range of GHz are similar to those in the range of MHz. So many researchers measured the tunable properties of the dielectric materials at the MHz frequency range [9–11]. 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. The dipoles formed from donor substitutes and barium vacancies are more easily oriented by an applied field [12]. Therefore, the BSCT thick films doped with 0.3 mol% $Yb_2O_3$ shows the highest tunability of 14.3%. However, the tunability of the specimens doped with more than 0.5 mol% $Yb_2O_3$ decreased due to increasing distortion and internal stress of the unit cell with excessive doping.

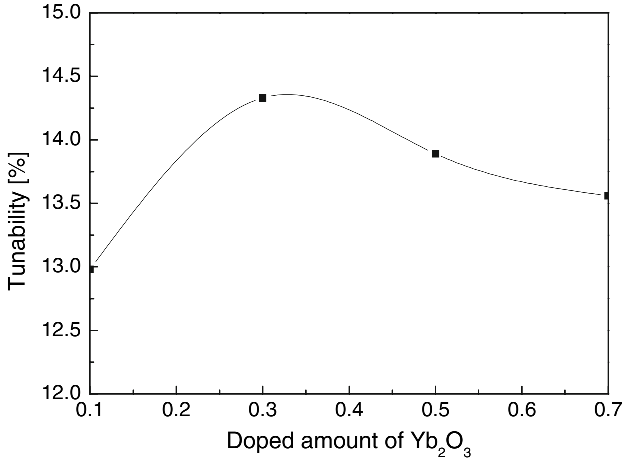

**Fig. 7** Tunability of BSCT thick films with various $Yb_2O_3$ contents at 1 MHz

## Conclusions

(Ba,Sr,Ca)TiO3 powders doped with $MnCO_3$ (0.1mol%) and $Yb_2O_3$ (0–0.7 mol%) were prepared by using the sol–gel method, and BSCT thick films were fabricated on the alumina substrates by the screen-printing method. All the BSCT thick films showed the typical XRD patterns of cubic perovskite polycrystalline structure and exhibited a uniform grain structure. The lattice constants of BSCT specimens decreased with increasing $Yb_2O_3$ contents. The BSCT thick films doped with 0.3 mol% $Yb_2O_3$ showed the high dielectric constant of 2,970 and the dielectric loss properties were independent of the $Yb_2O_3$ amount and were less than 0.01 at room temperature. The relative dielectric constant of all specimens decreased with increasing the applied DC voltage because the applied voltages suppress the displacement of ions inside the grains of paraelectric phase.

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