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Dielectric properties of B_2O_3 doped $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics at microwave frequency

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Abstract The microwave dielectric properties and the microstructures of $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics with B_2O_3 additions (0.25 and 0.5 wt%) prepared by conventional solid-state route have been investigated. The prepared $Sm(Co_{1/2}Ti_{1/2})O_3$ exhibited a mixture of Co and Ti showing 1:1 order in the B-site. Doping with B_2O_3 (up to 0.5 wt%) can effectively promote the densification of $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics with low sintering temperature. It is found that $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics can be sintered at 1,260 °C due to the grain boundary phase effect of B_2O_3 addition. At 1,290 °C, $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics with 0.5 wt% B_2O_3 addition possess a dielectric constant (ε_r) of 27.7, a $Q \times f$ value of 33,600 (at 9 GHz) and a temperature coefficient of resonant frequency (τ_f) of –11.4 ppm/ °C. The B_2O_3-doped $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics can find applications in microwave devices requiring low sintering temperature.

Introduction

Due to the development in mobile communication, mobile telephone systems, as well as in satellite broadcasting systems was rapidly, how to design the high quality devices is very important. In order to achieve miniaturization of the dimensions of the devices and for the system work with high efficiency and stability, many researches have been focusing on developing dielectric materials. Much research has been focused on developing dielectric materials with high quality factor ($Q \times f$), high dielectric constant (ε_r) and zero temperature coefficient of resonant frequency (τ_f) for use as dielectric resonators and microwave device substrates. High dielectric constant material can effectively reduce the size of resonators since the wavelength (λ) in dielectrics is inversely proportional to $\sqrt{\varepsilon_r}$ of the wavelength (λ_o) in vacuum $\left(\lambda = \lambda_0/\sqrt{\varepsilon_r}\right)$. The inverse of the dielectric loss $(Q = 1/\tan\delta)$ is required to be high for achieving prominent frequency selectivity and stability in microwave transmitter components and small temperature coefficient of the resonant frequency is required to ensure the stability of the microwave components at different working temperature. Several compounds such as $(Zr, Sn)TiO_4$, $Ba(Mg_{1/3}Ta_{1/3})O_3$ and $(Mg, Ca)TiO_3$ have therefore been developed [1–3]. $Ln(Mg_{1/2}Ti_{1/2})O_3$ (Ln = La, Sm, Nd, Dy, Y) ceramic has been widely used as a substrate for superconducting microwave devices since it provides a high quality factor, excellent lattice matching and a good matching for thermal expansion [4–6].

$Ln(Mg_{1/2}Ti_{1/2})O_3$ compositions which were measured quality factor ($Q \times f$) of the ceramic specimens was larger than 30,000 (GHz) and dielectric constant revealed between 22 and 27 have noncubic symmetry and the $GdFeO_3$-type structure [4]. Since $Sm(Mg_{1/2}Ti_{1/2})O_3$ has a dielectric constant (ε_r) of 25, a quality factor ($Q \times f$) of 65,500 (GHz) and a temperature coefficient of resonant frequency (τ_f) of –26 (ppm/ °C),

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it is one of $Ln(Mg_{1/2}Ti_{1/2})O_3$ compositions was determined to be suitable substrates for YBCO thin film and resonator used in microwave applications. In addition, because of the ion radius of Co^{+2} (0.082 nm) is similar to that of Mg^{+2} (0.078 nm), the ion of Mg^{+2} can be substituted by the ion of Co^{+2} to form $Sm(Co_{1/2}Ti_{1/2})O_3$ compositions. It also possess suitable microwave dielectric properties ($\varepsilon_r \sim 25.5$, $Q \times f \sim 76{,}000$ GHz, $\tau_f \sim -16.3$ ppm/ °C at sintering temperature of 1,360 °C) for applications in dielectric resonators [7]. However, the sintering temperatures of conventional microwave dielectric ceramics used for dielectric resonators, filters and other communication devices normally at lower then 1,300 °C. For practical applications, it is necessary to reduce the sintering temperature of $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics. Low melting glass addition, chemical processing and small particle sizes of the starting materials are generally advantageous to reduce the sintering temperature of dielectric materials [3, 8–10]. The first method using liquid phase sintering was found to effectively lower the firing temperature. However, it also decreased the microwave dielectric properties of dielectric resonators. The chemical process often required a flexible, expensive and time consuming procedure. In the past, liquid phase flux such as B_2O_3 and CuO were added to lower the sintering temperature of ceramics [11, 12]. In this paper, B_2O_3 was added to further lower the sintering temperature. The crystalline phases, the microstructures and the microwave dielectric properties of B_2O_3-doped $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics were investigated.

Experimental method

Sample of $Sm(Co_{1/2}Ti_{1/2})O_3$ was prepared using conventional solid-state method from individual high-purity oxide powders(>99.9%): Sm_2O_3, CoO and TiO_2. The starting materials were mixed according to a stoichiometric ratio to synthesize $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics. The powders were ground in distilled water for 12 h in a ball mill with agent balls. The mixture was dried at 100 °C, and thoroughly milled before it was calcined at 1,100 °C for 2 h. The calcined powder $Sm(Co_{1/2}Ti_{1/2})O_3$ was ground and sieved through 100-mesh screen. Phase formation of $Sm(Co_{1/2}Ti_{1/2})O_3$ was confirmed using X-ray diffraction (XRD). The calcined powders with different amount of B_2O_3 additions were then re-milled for 12 h with PVA solution as a binder. The milled powders were pressed into disk 11 mm in diameter and 5 mm in thickness. A pressing pressure of 2,000 kg/cm^2 was used for all samples. The pellets were sintered at temperatures 1,200–1,350 °C for 4 h in the air. The heating rate and the cooling rate were both controlled at 10 °C /min.

The X-ray diffraction (XRD, Rigaku D/Max III.V) data of powder and bulk samples were collected using Cu Kα radiation (at 30 Kv and 20 mA) and a graphite monochromator in the 2θ range of 20–60°. The microstructural observations and analysis of sintered surface were performed using a scanning electron microscopy (SEM, Philips XL-40FEG) and an energy dispersive X-ray spectrometer (EDS). The density of the sintered specimens, as a function of sintering temperature, was measured by the liquid Archimedes method using distilled water as the liquid.

The dielectric constants (ε_r) and $Q \times f$ values at microwave frequencies were measured using the Hakki–Coleman dielectric resonator method, as modified and improved by Courtney [13, 14]. The dielectric resonator was positioned between two brass plates such like cavity. Microwave dielectric properties of sintered samples were measured by HP8757D network analyzer and HP8350B sweep oscillator. For temperature coefficient of resonant frequency (τ_f), the technique is the same as that of quality factor measurement. The test cavity is placed over a thermostat and the temperature range used is +25 °C to +80 °C. The τ_f (ppm/ °C) is calculated by noting the change in resonant frequency (Δf) by,

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (1)$$

where f_1 is resonant frequency at T_1 and f_2 is the resonant frequency at T_2.

Results and discussion

Figure 1 shows the XRD patterns of B_2O_3-doped $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics at different sintering temperatures (1,200–1,350 °C). Homogeneous $Sm(Co_{1/2}Ti_{1/2})O_3$ phase with an orthorhombic structure could be obtained. Similar XRD patterns were detected for the $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics with various B_2O_3 addition at sintering temperatures 1,200–1,350 °C. Second phase was not observed at the level of various B_2O_3 additions since detection of a minor phase by X-ray is extremely difficult. In addition, identical XRD patterns were observed for the ceramics irrespective of the amount of B_2O_3 additions.

The SEM photographs of B_2O_3-doped $Sm(Co_{1/2}Ti_{1/2})O_3$ at sintering temperatures of 1,200–1,350 °C are shown in Fig. 2. The grain size increased with the increase of sintering temperature as well as amount of

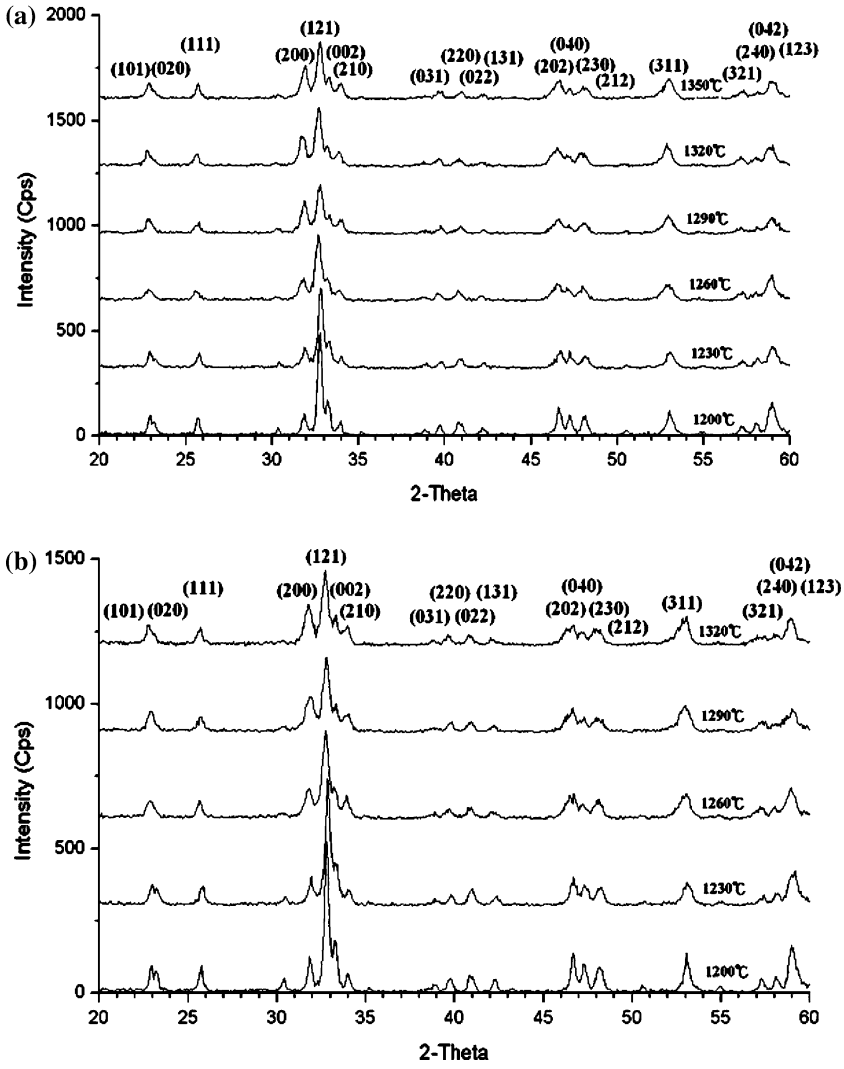

Fig. 1 X-ray diffraction patterns of $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics at different sintering temperatures (**a**) 0.25 wt% B_2O_3 addition (**b**) 0.5 wt% B_2O_3 addition

B_2O_3 addition due to the sintering aid. In addition, porous specimens were observed for $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics at temperatures 1,200 and 1,230 °C with B_2O_3 additions. However, rapid grain growth and grain boundary phases appeared for $Sm(Co_{1/2}Ti_{1/2})O_3$ specimens with B_2O_3 additions at sintering temperatures higher than 1,320 °C. This may directly affect the microwave dielectric properties of the ceramic samples.

The density of B_2O_3-doped $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics at different sintering temperatures is shown in Fig. 3. The density initially increased with increasing sintering temperature due to enlarged grain size as observed in Fig. 2. On the other hand, the density is also related to the porosity and increased with the decreased of porosity. After reaching the maximum at 1,290 °C with 0.5 wt% doped B_2O_3 addition, it decreased thereby owing to the rapid grain growth as well as the grain boundary phases. It seemed that B_2O_3 did contribute to the densification of $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics at low temperatures. The maximum density was found to be 6.96 g/cm^3 for specimen with 0.5 wt% B_2O_3 addition at 1,290 °C. It is difficult to synthesize ceramics with ultra-high relative density by the conventional solid-state method unless it is augmented by other methods, such as chemical processing.

Figure 4 demonstrates the dielectric constants of $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics with different amounts of B_2O_3 additions as functions of sintering temperatures. The relationships between dielectric constant and sintering temperature reveal the same trend as that for density and sintering temperature since higher density represents lower porosity. The dielectric constants slightly increased with increasing sintering temperature. The increase in the ε_r value could be explained owing to higher densities. However, an observable degradation in the ε_r value appeared at the higher sintering temperature with various B_2O_3 additions. The dielectric constants varied from 27.7 to 21.4 as the amount of B_2O_3 addition increased from

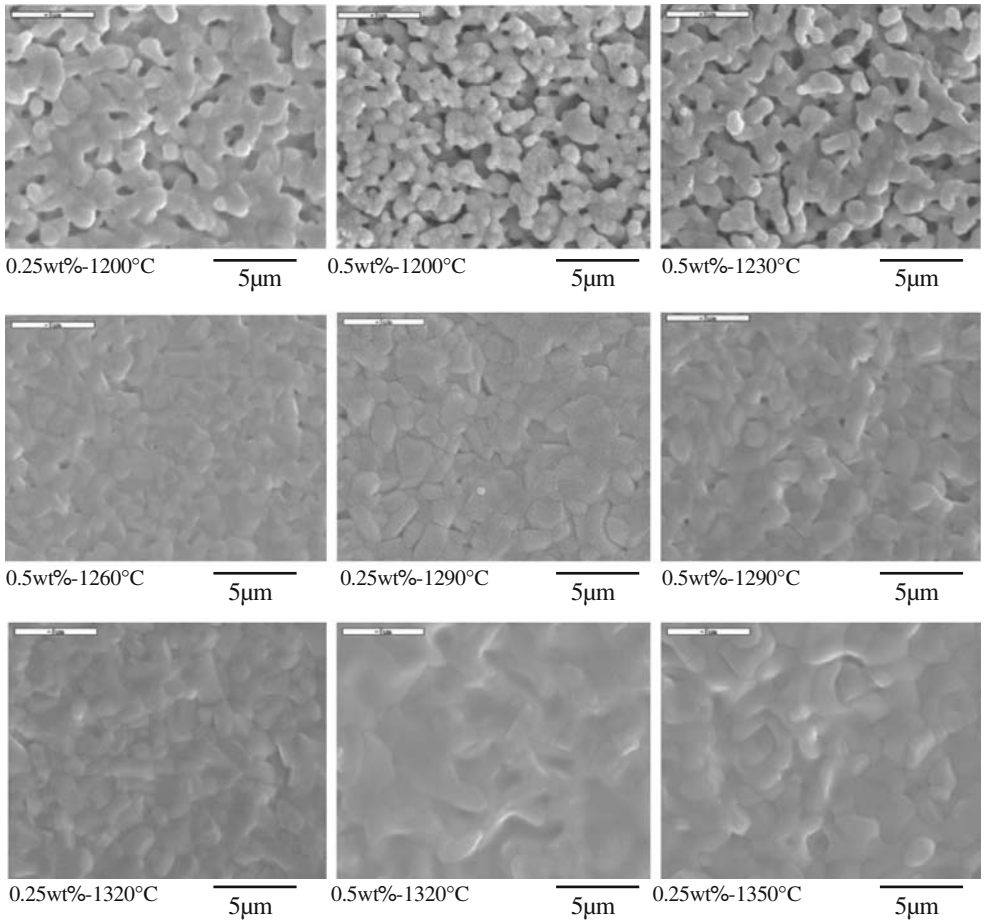

Fig. 2 SEM photographs of $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics with different B_2O_3 additions at different sintering temperatures

0.25 to 0.5 wt%. The highest dielectric constant was obtained for 0.5 wt% B_2O_3-doped $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics sintered at 1,290 °C. The variation of the ε_r value was mainly a result from the density of the specimen.

Figure 5 shows the $Q \times f$ values of B_2O_3-doped $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics with various sintering temperatures. The microwave dielectric loss is mainly caused not only by the lattice vibrational modes, but also by the pores and the secondary phases [15]. With 0.5 wt% B_2O_3 addition, $Q \times f$ increased from 8,400 to 33,600 GHz as the sintering temperature increased from 1,200 to 1,290 °C for 4 h and thereafter decreased. The decrease in $Q \times f$ was due to the rapid grain growth as observed in Fig. 2. Abnormal grains as well as larger grain boundary phases degraded the $Q \times f$ values of the as-sintered samples with B_2O_3 addition at high sintering temperatures. On the other hand, it may due to the small grain size and porous specimens were observed at the lower sintering temperature, and this is the reason causing $Q \times f$ value to be diminished. However, the relationships between $Q \times f$ values and sintering temperatures reveal the same trend as those between densities and sintering temperatures. Relative density also plays an important role in controlling the dielectric loss and this has been shown for other microwave dielectric materials. On the other hand, the sintering temperatures of the optimum $Q \times f$ value for various B_2O_3 additions were decreased with increasing B_2O_3 contents. It may ascribed the reduction of sintering temperature of the optimum $Q \times f$ value to the dense and uniform grain size were produced at the lower sintering temperature with increased B_2O_3 contents as also observed in Fig. 2. With 0.5 wt% B_2O_3 addition, an excellent $Q \times f$ value of 33,600 (GHz) was obtained for $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics sintered at 1,290 °C for 4 h. The quality factors of B_2O_3-doped $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics at low sintering temperatures were relatively lower than that of pure $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics due to the grain boundary phase and abnormal grains.

The temperature coefficients of resonant frequency (τ_f) of B_2O_3-doped $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics at different sintering temperatures are illustrated in Fig. 6. The temperature coefficient of resonant frequency is well known related to the composition, the additives and the second phase of the material. The τ_f value, as presented, was a function of the B_2O_3 content. It varied from average –16.7 to –10.2 ppm/ °C as the amount of

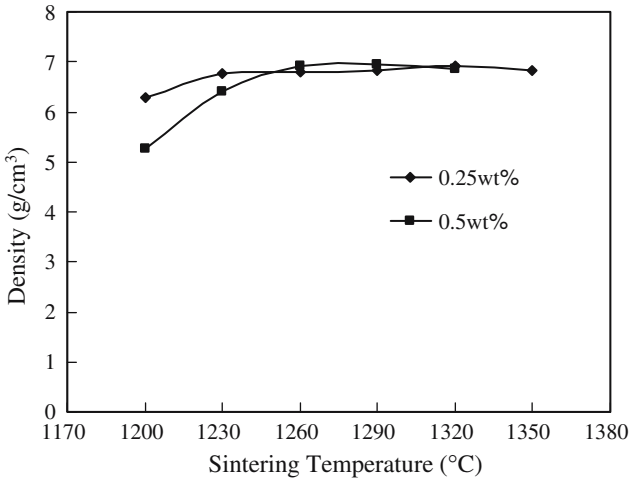

Fig. 3 Dependence of density on sintering temperature of $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics with various B_2O_3 additions

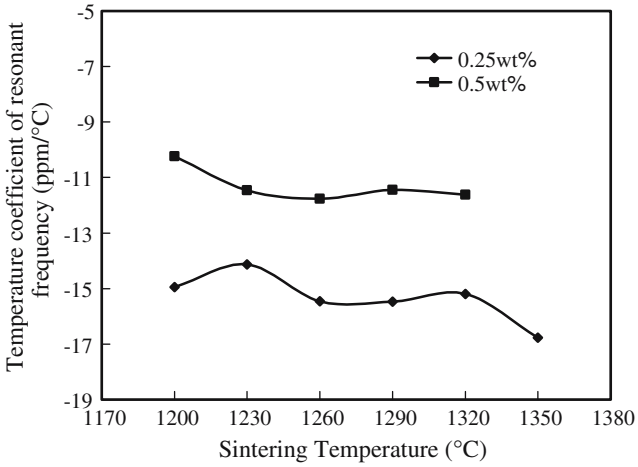

Fig. 6 Dependence of τ_f value on sintering temperature of $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics with various B_2O_3 additions

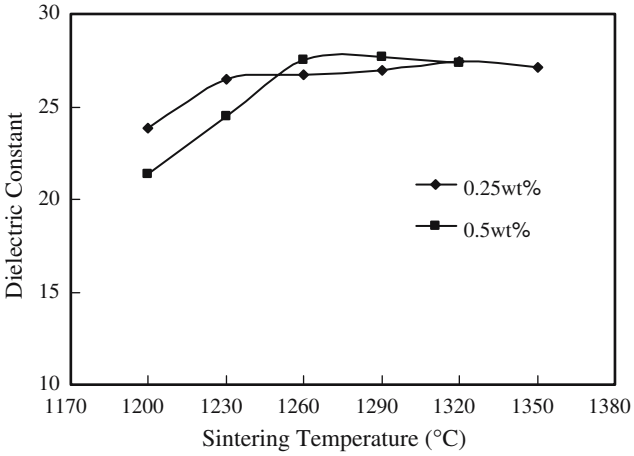

Fig. 4 Dependence of dielectric constant on sintering temperature of $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics with various B_2O_3 additions

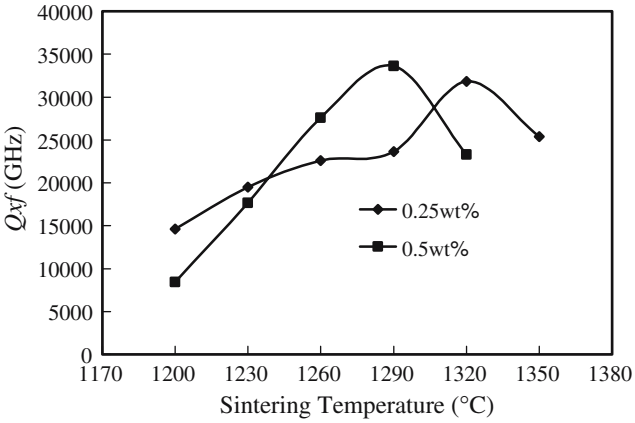

Fig. 5 Dependence of quality factor ($Q \times f$) on sintering temperature of $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics with various B_2O_3 additions

B_2O_3 addition increased from 0.25 to 0.5 wt%. Significant change was not observed in the τ_f value with fixed B_2O_3 addition at different sintering temperatures. However, it revealed the τ_f values were varied toward the positive direction with increasing B_2O_3 content due to the formation of the grain boundary phase. It implies that the τ_f value was not sensitive to the sintering temperature.

Conclusion

The dielectric properties of B_2O_3-doped $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics have been investigated. The B_2O_3 addition was employed as a sintering aid to lower the firing temperature of the $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics. A sintering temperature reduction (about 100 °C) can be achieved by adding B_2O_3 to the $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics. The dielectric constants saturated at 26–27 with the higher sintering temperatures (1,260–1,350 °C). The quality factor of B_2O_3-doped $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics were relatively lower than the value of purity $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics due to grain boundary phases and abnormal grains. The temperature coefficient of the resonant frequency was varied toward 0 ppm/ °C with increasing the B_2O_3-doped values and has a small amount variation with different sintering temperatures. With 0.5 wt% B_2O_3 addition, a dielectric constant of 27.7, a $Q \times f$ value of 33,600 (GHz) and a τ_f value of –11.4 ppm/ °C were obtained for $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics at 1,290 °C for 4 h. The B_2O_3-doped $Sm(Co_{1/2}Ti_{1/2})O_3$ ceramics can find applications in microwave devices requiring low sintering temperatures.

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