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Microwave dielectric properties of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics with a zero temperature coefficient of resonant frequency

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ABSTRACT

High-quality $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics were prepared by solid-state reaction. The products were characterized by scanning electron microscopy, X-ray diffraction, and network analyzer.

$(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ has a dielectric constant (ε_r) of ~20, a high-quality factor ($Q\times f$) of ~163,560 GHz, and a temperature coefficient of resonant frequency (τ_f) of ~−65 ppm/°C. To produce a temperature-stable material, $Ca_{0.8}Sm_{0.4/3}TiO_3$, which has a large positive τ_f value of 400 ppm/°C, was added to $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$. $0.85(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.15Ca_{0.8}Sm_{0.4/3}TiO_3$ has an excellent combination of microwave dielectric properties: $\varepsilon_r \sim 29.5$, $Q\times f \sim 65{,}000$ (at 9 GHz), and $\tau_f \sim 1$ ppm/°C sintered at 1175 °C, and can be utilized in the fabrication of microwave devices.

1. Introduction

Wireless telecommunications is perhaps the sector of electronic industry showing the more dramatic growth in the past two decades. The use of ceramic materials in the fabrication of modern high-frequency filters and resonators has stimulated the search for new low-cost materials for technological applications. The improvement of dielectric materials has been focused on the tailoring of systems showing high unloaded quality factors (Q), high dielectric permittivity (ε_r) and near-zero temperature coefficients of the resonant frequency (τ_f), because these qualities are necessary to decrease the size of the devices and assure the frequency stability and selectivity of the components under different atmospheric conditions. Nevertheless to achieve these requirements it is usually necessary to reach a compromise [1,2]. The unique electrical properties of ceramic dielectric resonators have revolutionized the microwave-based wireless communications industry by reducing the size and cost of filter and oscillator components in circuit systems. The use of dielectric resonators makes the size reduction of microwave components possible. Requirements for these dielectric resonators are a high dielectric constant, a low dielectric loss ($Q > 5000$, where $Q = 1/\tan\delta$), and a near-zero temperature coefficient of resonant frequency (τ_f) [3]. The high-quality factor (inverse of the dielectric loss, $Q = 1/\tan\delta$) plays a prominent role as $Q\times f$ is almost constant in the microwave region.

$0.95MgTiO_3$–$0.05CaTiO_3$ ceramic has an $\varepsilon_r \sim 21$, a $Q\times f \sim 56{,}000$ (at 7 GHz), and a zero τ_f value [4]. However, it requires sintering temperatures as high as 1400–1450 °C. For practical applications, their sintering temperature needs to be reduced [5–9]. Replacing $MgTiO_3$ by $(Mg_{0.95}Zn_{0.05})TiO_3$ ($\varepsilon_r \sim 17.05$, $Q\times f \sim 264{,}000$ GHz, $\tau_f \sim -40.31$ ppm/°C), an even better combination of microwave dielectric properties can be achieved. For example, when sintered at 1200 °C, $(Mg_{0.7}Zn_{0.3})TiO_3$ has an $\varepsilon_r \sim 19.8$, a $Q\times f \sim 142{,}000$ GHz, and $\tau_f \sim -66$ ppm/°C [10]. With the partial replacement $(Mg_{0.7}Zn_{0.3})$ by Co, $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ had excellent dielectric properties with an $\varepsilon_r \sim 20$, $Q\times f \sim 163{,}560$ GHz, and a $\tau_f \sim -65$ ppm/°C after being sintered at a low sintering temperature of 1200 °C [10]. The $Ca_{0.8}Sm_{0.4/3}TiO_3$ has a high ε_r of around 120, a $Q\times f$ value higher than 13,800 GHz and a τ_f value of 400 ppm/°C [11].

The present work thus aims to investigate the microstructures and microwave dielectric of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sm_{0.4/3}TiO_3$.

2. Experimental procedure

The starting materials were high-purity oxide powders (>99.9%): MgO, ZnO, TiO_2, CoO, CaO, and Sm_2O_3. The powders were separately prepared according to the desired stoichiometry of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ and $Ca_{0.8}Sm_{0.4/3}TiO_3$. They were then ground in distilled water for 12 h in a ball mill with agate balls. The prepared powders were dried and calcined at 1000 °C and 1100 °C for 4 h in air. After calcination, the calcined powders were mixed according to the molar fraction $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sm_{0.4/3}TiO_3$ and then remilled for 12 h. A fine

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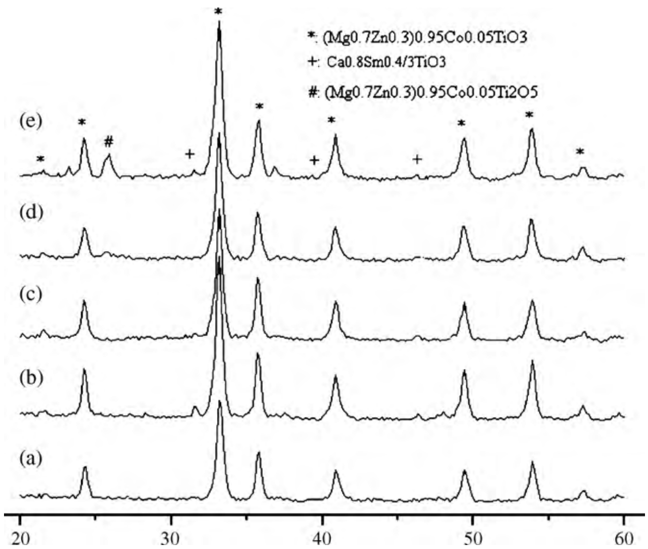

Fig. 1. X-ray diffraction patterns of $0.85(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.15Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics sintered at various temperatures for 4 h: (a)1140 °C, (b) 1175 °C, (c) 1200 °C, (d) 1225 °C and (e) 1250 °C.

powder with 3 wt% of a 10% solution of polyvinyl alcohol (PVA 500, Showa, Japan) used as a binder was pressed into pellets, 11 mm in diameter and 5 mm thick, under a pressure of 200 MPa. The pellets were sintered at temperatures of 1140–1250 °C for 4 h in air. The heating and the cooling rates were both set at 10 °C/min.

The crystalline phases of the calcined powder and the sintered ceramics were identified using X-ray diffraction pattern analysis. The microstructure observations and analysis of sintered surface were performed using a scanning electron microscope (SEM, Philips XL–40FEG). Energy dispersive spectroscopy (EDS) was used to identify the existence of second phases. The bulk densities of the sintered pellets were measured using the Archimedes method. The dielectric constant (ε_r) and the quality factor values (Q) at microwave frequencies were measured using the Hakki–Coleman [12] dielectric resonator method under TE011 and TE01σ modes as modified and improved by Courtney [13]. The dielectric resonator was positioned between two brass plates. A system combined with an HP8757D network analyzer and an HP8350B sweep oscillator was employed in the measurement. The same technique was applied in measuring the temperature coefficient of resonant frequency (τ_f). The test set was placed over a thermostat in the temperature range of +25–80 °C. The τ_f value (ppm/°C) was calculated by noting the change in resonant frequency (Δf):

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

where f_1 and f_2 represent the resonant frequencies at T_1 and T_2, respectively.

3. Results and discussion

Fig. 1 shows the XRD patterns of the $0.85(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–0.15 $Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramic sintered at various temperatures for 4 h. The XRD patterns showed that peaks indicating the presence of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ as the main crystalline phase, in association with $Ca_{0.8}Sm_{0.4/3}TiO_3$ as minor phases. According to the XRD patterns, the $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ phase exists in these specimens. The X-ray diffraction patterns of the $0.85(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.15Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramic systems have not been changed significantly with sintering temperatures in the range of 1140–1250 °C. The XRD patterns show peaks indicating the presence of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ as the main crystalline phase, a minor phase of $Ca_{0.8}Sm_{0.4/3}TiO_3$. The formation of mixed phases in the $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramic system was due to structural differences; therefore, a solid solution could not be obtained. The XRD patterns of the $0.85(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.15Ca_{0.8}Sm_{0.4/3}TiO$ ceramic did not significantly change with sintering temperature in the range of 1140–1225 °C. However, Fig. 1 shows that new phases such as $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}Ti_2O_5$ was developed with firing at higher temperatures. These new phases are believed to occur from vigorous ZnO volatilization particularly at the temperature of 1250 °C.

The surface microstructure photographs of $0.85(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.15Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics for various sintering temperatures are presented in Fig. 2. Porous microstructures were observed at 1140 °C; the grains, however, started to grow at 1175 °C and a significant increase in the grain size was observed at 1175 °C. Inhomogeneous grain growth was observed at temperatures higher than 1200 °C, which might degrade the microwave dielectric properties of the ceramics.

The energy dispersive X-ray (EDX) analysis was used in combination with scanning electron microscopy to distinguish every grain for $0.85(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.15Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics sintered at 1175 °C, as shown in Fig. 3(a). The EDX datum and data of corresponding spots A an B were showed in Fig. 3(b), respectively. The grain morphology of well developed $0.85(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.15Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics could be grouped into two types: both large grains (spot A), indicating Mg–Ti phase, were $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$, and small cubic-shape grains (spot B) were $Ca_{0.8}Sm_{0.4/3}TiO_3$. In contract to that of pure $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$, $(Ca_{0.8}Sm_{0.4/3})TiO_3$ shows a lower sintering temperature. It is because the grain size of $Ca_{0.8}Sm_{0.4/3}$ TiO_3 is smaller than that of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ and adding $Ca_{0.8}Sm_{0.4/3}TiO_3$ to $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ would benefit the densification of the ceramics.

Fig. 4 shows the bulk densities of the $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics sintered at various temperatures for 4 h. With increasing temperature, the bulk density increased to a maximum value of 3.95 g/cm^3 at 1175 °C, and then it decreased. The reduction of density due to the abnormal grain growth is shown in Fig. 2. The variation of ε_r was consistent with that of density. The dielectric constant also increased with sintering temperature. After reaching a maximum at 1175 °C, it decreased.

Fig. 5 shows the dielectric constants curves of the $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramic system at various sintering temperatures for 4 h. The relationship between ε_r values and sintering temperature shows the same trend as that between density and sintering temperature since higher density means lower porosity. The dielectric constant slightly increased with increasing sintering temperature. ε_r values of $0.85(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.15Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics increased from 28 to 29.5 when the sintering temperature was increased from 1140 to 1175 °C. A maximum ε_r value of 39.2 was obtained $0.6(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.4Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics sintered at 1175 °C for 4 h.

Microwave dielectric loss can be divided into intrinsic loss and extrinsic loss. Intrinsic losses are mainly caused by lattice vibration modes while extrinsic losses are dominated by second phases, oxygen vacancies, grain sizes and densification or porosity. Interfacial polarization is thought to play an important role in porous materials. The quality factor values ($Q\times f$) of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramic at various sintering temperatures are shown in Fig. 6. With increasing sintering temperature, the $Q\times f$ value increased to a maximum value and then decreased. A maximum $Q\times f$ value of 87,000 GHz was obtained for $0.9(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.1Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramic at 1175 °C. The degradation of the $Q\times f$ value can be attributed to abnormal grain growth at higher sintering temperatures, as shown in Fig. 2. The microwave dielectric loss is mainly caused by the lattice vibrational modes, pores, second phases, impurities, and lattice defects. Relative density also plays an important role in

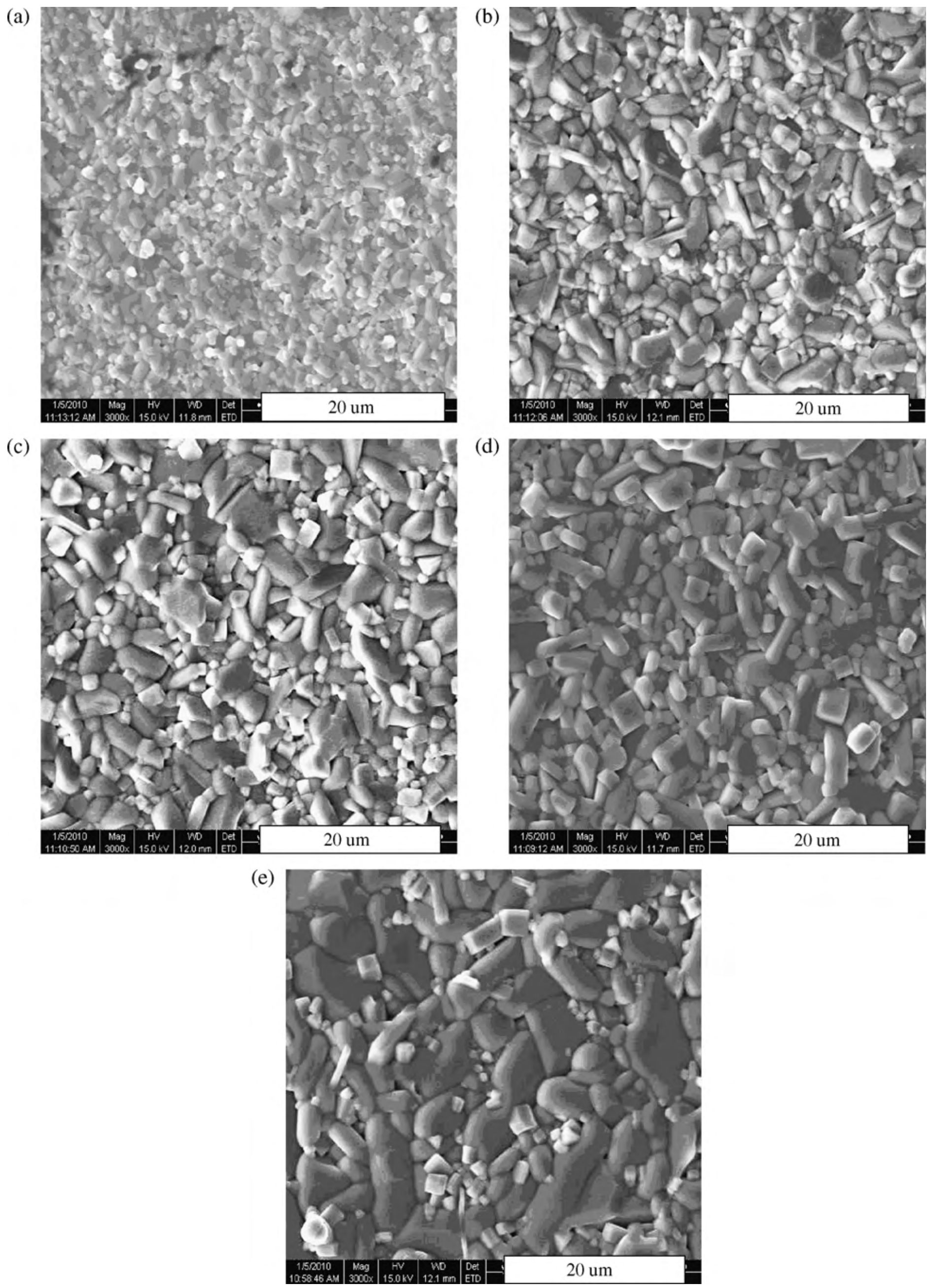

Fig. 2. SEM micrographs of $0.85(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.15Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics sintered at (a) 1140 °C, (b) 1175 °C, (c) 1200 °C, (d) 1225 °C, and (e) 1250 °C for 4 h.

controlling dielectric loss, as has been shown for other microwave dielectric materials.

Fig. 7 shows the τ_f values of the $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics sintered at various sintering temperatures. The temperature coefficient of resonant frequency (τ_f) is known to be governed by the composition, the additives, and the second phase of the material. Because the τ_f values of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ and $Ca_{0.8}Sm_{0.4/3}TiO_3$ are −65 and 400 ppm/°C, respectively, increasing $Ca_{0.8}Sm_{0.4/3}TiO_3$ content makes the τ_f value more positive. This implies that a zero τ_f value can be achieved by tuning the amount of $Ca_{0.8}Sm_{0.4/3}TiO_3$ content. In fact, with $x = 0.85$, a near-zero τ_f value was achieved for the $0.85(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.15Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramic system sintered at 1175 °C for 4 h.

Table 1 shows the microwave dielectric properties of the $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramic system sintered at 1175 °C for 4 h. When the $(1-x)$ value increased from 0.1 to 0.4, the τ_f values of the $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramic system changed from −20 to 75 ppm/°C. The τ_f curves went through zero, which indicates that a zero τ_f value can be obtained by appropriately adjusting the x value of the

Table 1
Microwave dielectric properties of the $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics system sintered at 1175 °C for 4 h.

$(1-x)$ value	Bulk density (g/cm^3)	ε_r	$Q \times f$ (GHz)	τ_f (ppm/°C)
0.1	3.85	27.2	71,000	−20
0.15	3.96	29.5	65,000	1
0.3	4	35.1	61,000	32
0.4	4.1	39.2	53,000	75

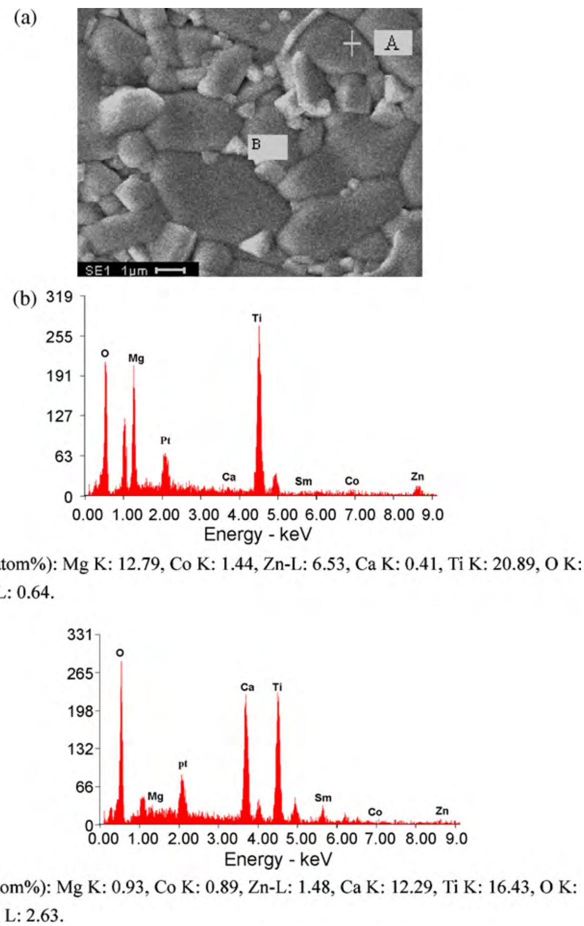

Fig. 3. (a) The marks of SEM for the. $0.85(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.15Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics sintered at 1175 °C and (b) EDX data of $0.85(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.15Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics for spots A and B.

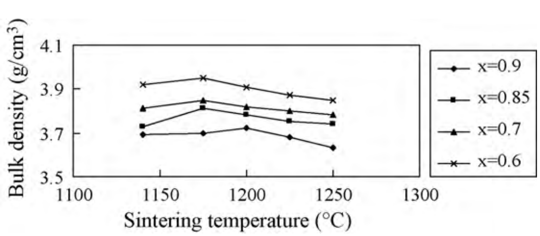

Fig. 4. Bulk density of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics sintered at various temperatures.

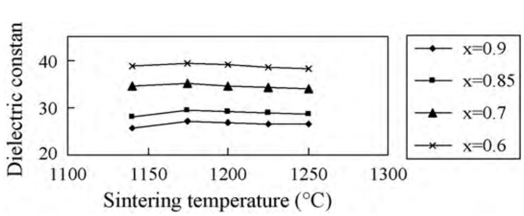

Fig. 5. Dielectric constant's curves of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics at different sintering temperatures for 4 h.

$x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramic system. With $x = 0.85$, the $0.85(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.15Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramic system shows good temperature stability with $\tau_f \sim 1$ ppm/°C. However, when the $Ca_{0.8}Sm_{0.4/3}TiO_3$ content was increased, the $Q \times f$ value decreased because the $Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramic has a low $Q \times f$ value of 13,800 GHz.

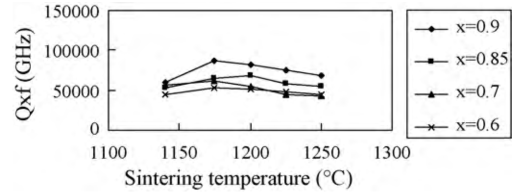

Fig. 6. $Q \times f$ and τ_f values of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics sintered at various temperatures.

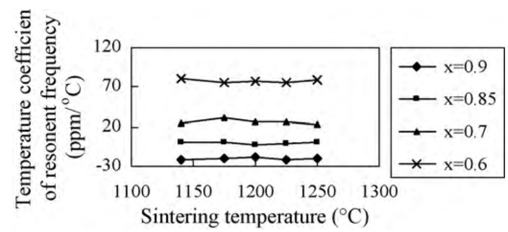

Fig. 7. τ_f values of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sm_{0.4/3}TiO_3$ system sintered at different temperatures for 4 h.

4. Conclusion

In this paper, $Ca_{0.8}Sm_{0.4/3}TiO_3$ was added to $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ to adjust τ_f values and improve the dielectric constant. $0.85(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.15Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramic exhibited mixed phases of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ as the main phase with some minor phases of $Ca_{0.8}Sm_{0.4/3}TiO_3$. With the partial replacement of $(Mg_{0.7}Zn_{0.3})$ by Co, $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ had excellent dielectric properties with an $\varepsilon_r \sim 20$, $Q \times f \sim 163{,}560$ GHz, and a $\tau_f \sim -65$ ppm/°C after being sintered at a low temperature of 1200 °C. The $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramic system showed mixed phases of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ as the main crystalline phase, a minor phase of $Ca_{0.8}Sm_{0.4/3}TiO_3$. At 1175 °C, the $0.85(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.15Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramic demonstrated excellent microwave dielectric properties: $\varepsilon_r \sim 27.2$, $Q \times f \sim 65{,}000$ GHz (at 9 GHz), and $\tau_f \sim 1$ ppm/°C. Their excellent dielectric properties make the $0.85(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.15Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramic capable in the application of microwave devices.

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