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Microwave dielectric properties of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sr_{0.2}TiO_3$ ceramics with a zero temperature coefficient of resonant frequency

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ABSTRACT

The microwave dielectric properties and microstructures of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sr_{0.2}TiO_3$ ceramics prepared using a mixed oxide route were investigated. $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ 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, $Ca_{0.8}Sr_{0.2}TiO_3$, which has a large positive τ_f value of 990 ppm/°C, was added to $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$. The temperature coefficient of resonant frequency increased with increasing $Ca_{0.8}Sr_{0.2}TiO_3$ content, going through zero at $x = 0.95$. The microwave dielectric material $0.95(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.05Ca_{0.8}Sr_{0.2}TiO_3$ has an excellent combination of microwave dielectric properties: $\varepsilon_r \sim 22.5$, $Q \times f \sim 90{,}000$ (at 9 GHz), and $\tau_f \sim 0.1$ ppm/°C sinter at 1150 °C. It is proposed as a candidate material for ISM band components and GPS antennas.

1. Introduction

Several research groups have developed microwave dielectric resonators (DRs) with satisfactory dielectric properties. Ceramic materials for DR applications should have high-quality factor (Q), high relative permittivity (ε_r) and the stability of these parameters in the working temperature and frequency ranges [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. For instance, low-loss dielectrics with dielectric constants in the 21 s have become the most popular materials used for GPS patch antennas, WLAN band-pass filters, and even for 5.8 GHz ISM band filters.

$MgTiO_3$-based ceramics, which have low dielectric loss, have been intensively studied for years. $MgTiO_3$–$CaTiO_3$ ceramics made of a mixture of modified α-Al_2O_3 structured magnesium titanate ($MgTiO_3$: $\varepsilon_r \sim 17$, $Q \times f \sim 160{,}000$ (at 9 GHz), and $\tau_f \sim -50$ ppm/°C) [4] and perovskite structured calcium titanate ($CaTiO_3$: $\varepsilon_r \sim 170$, $Q \times f \sim 3600$ (at 7 GHz), and $\tau_f \sim 800$ ppm/°C) [5] have been applied in dielectric resonators and patch antennas. With a ratio of Mg:Ca = 95:5, $0.95MgTiO_3$–$0.05CaTiO_3$ 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 [6–9]. Since the ionic radius of Zn^{2+} (0.083 nm) is similar to that of Mg^{2+} (0.078 nm), Mg^{2+} ions can be substituted by Zn^{2+} ions to form $(Mg, Zn)TiO_3$ compositions. Heavily Zn-substituted $MgTiO_3$, which leads to the formation of $(Mg, Zn)TiO_3$ solid solution, has been shown to have a relatively low sintering temperature. 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].

In stead of $SrTiO_3$, $(Ca_{0.8}Sr_{0.2})TiO_3$ ceramics ($\varepsilon_r \sim 181$, $Q \times f \sim 8300$ GHz, $\tau_f \sim 991$ ppm/°C [11], having a much higher $Q \times f$ than that of $SrTiO_3$, was chosen as a τ_f compensator for $Ca_{0.8}Sr_{0.2}TiO_3$. To produce a temperature-stable material, $Ca_{0.8}Sr_{0.2}TiO_3$, which has a large positive τ_f value of 990 ppm/°C, was added to $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ [10].

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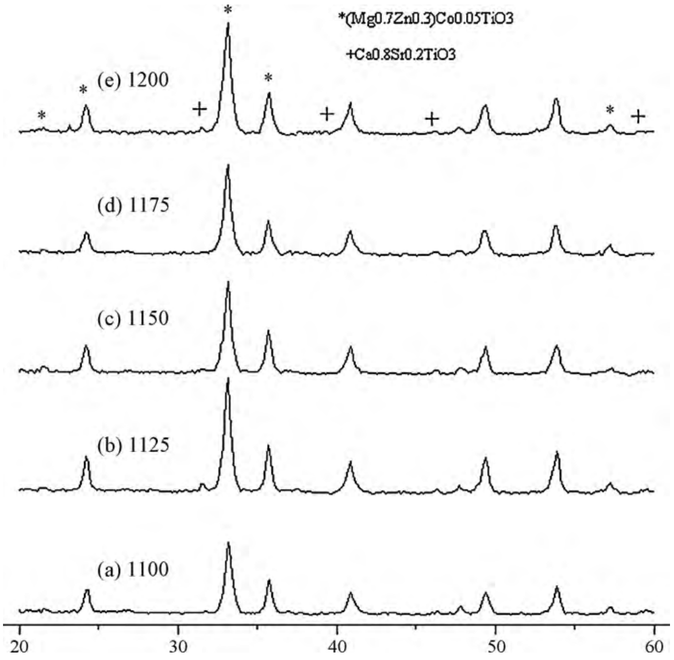


Fig. 1. X-ray diffraction patterns of $0.95(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.05Ca_{0.8}Sr_{0.2}TiO_3$ ceramics sintered at various temperatures for 4 h.

In this study, the microwave dielectric properties of the $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sr_{0.2}TiO_3$ ceramic system were analyzed using densification, X-ray diffraction (XRD) patterns, and microstructures. The correlation between the microstructure and the $Q \times f$ value was also investigated.

2. Experimental procedures

The starting materials were high-purity oxide powders (>99.9%): MgO, ZnO, TiO_2, CoO, CaO, and $SrCO_3$. 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 $Ca_{0.8}Sr_{0.2}TiO_3$. 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 $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sr_{0.2}TiO_3$ and then remilled for 12 h. A fine 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 1100–1200 °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 by 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 comprising of an HP8757D network analyzer and an HP8350B sweep oscillator was employed in the measurement. An identical 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 from +25 °C to +80 °C. The τ_f value (ppm/°C) can be 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 $0.95(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.05\ Ca_{0.8}Sr_{0.2}TiO_3$ 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 $Ca_{0.8}Sr_{0.2}TiO_3$ as minor phases. It is understood that crystal structures of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ and $Ca_{0.8}Sr_{0.2}TiO_3$ are rhombohedral (ICDD-PDF #01-073-7752) and orthorhombic (ICDD-PDF #00-022-0153), respectively. According to the XRD patterns, the $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ phase exists in these specimens. X-ray diffraction patterns of $0.95(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.05\ Ca_{0.8}Sr_{0.2}TiO_3$ ceramics system have not been changed significantly with sintering temperatures in the range 1100–1200 °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 $Ca_{0.8}Sr_{0.2}TiO_3$. The formation of mixed phases in the $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sr_{0.2}TiO_3$ ceramic system was due to structural differences; therefore, a solid solution could not be obtained. The XRD patterns of the $0.95(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.05Ca_{0.8}Sr_{0.2}TiO_3$ ceramic did not significantly change with sintering temperature in the range 1100–1200 °C.

SEM photographs of $0.95(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.05Ca_{0.8}Sr_{0.2}TiO_3$ ceramic for various sintering temperatures are presented in Fig. 2. Porous microstructures were observed at 1100 °C the grains; however, started to grow at 1150 °C and a significant increase in the grain size was observed at 1175 °C. Inhomogeneous grain growth was observed at temperatures higher than 1150 °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 $0.95(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.05\ Ca_{0.8}Sr_{0.2}TiO_3$ ceramic sintered at 1200 °C, as shown in Fig. 3(a). The EDX datum and data of corresponding spots A–B were showed in Fig. 3(b), respectively. The grain morphology of well developed $0.95(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.05\ Ca_{0.8}Sr_{0.2}TiO_3$ 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 $(Ca_{0.8}Sr_{0.2})TiO_3$. The EDX evidences are in agreement with the XRD results obtained from $0.95(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.05\ Ca_{0.8}Sr_{0.2}TiO_3$ ceramics. In contract to that of pure $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$, $(Ca_{0.8}Sr_{0.2})TiO_3$ shows a lower sintering temperature. It is because the grain size of $(Ca_{0.8}Sr_{0.2})TiO_3$ is smaller than that of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ and adding $(Ca_{0.8}Sr_{0.2})TiO_3$ 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 $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sr_{0.2}TiO_3$ ceramics sintered at various temperatures for 4 h. With increasing temperature, the bulk density increased to a maximum value of 3.8 g/cm^3 at 1150 °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 1150 °C, it decreased.

Fig. 5 shows the dielectric constants curves of the $x(Mg_{0.7}Zn_{0.3})0.95Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sr_{0.2}TiO_3$ ceramics at various sintering temperatures for 4 h. The relationship between ε_r values and sintering temperature revealed 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 $0.95(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.05\ Ca_{0.8}Sr_{0.2}TiO_3$ ceramics increased from 21.27 to 22.5 when the sintering temperature was increased from 1100 to 1150 °C. A maximum ε_r value of 26.7 was obtained $0.85(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.15Ca_{0.8}Sr_{0.2}TiO_3$ ceramics sintered at 1150 °C for 4 h.

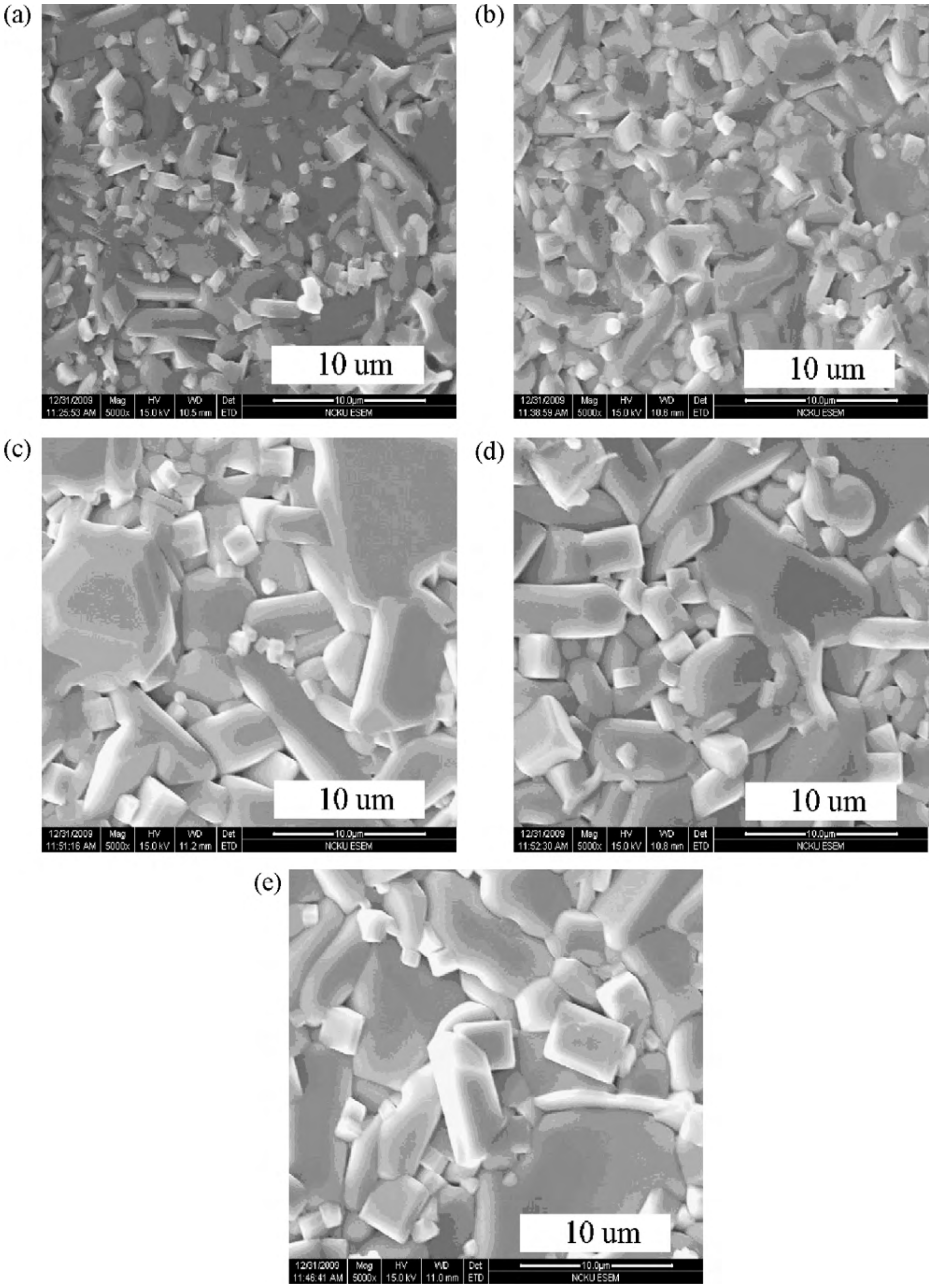
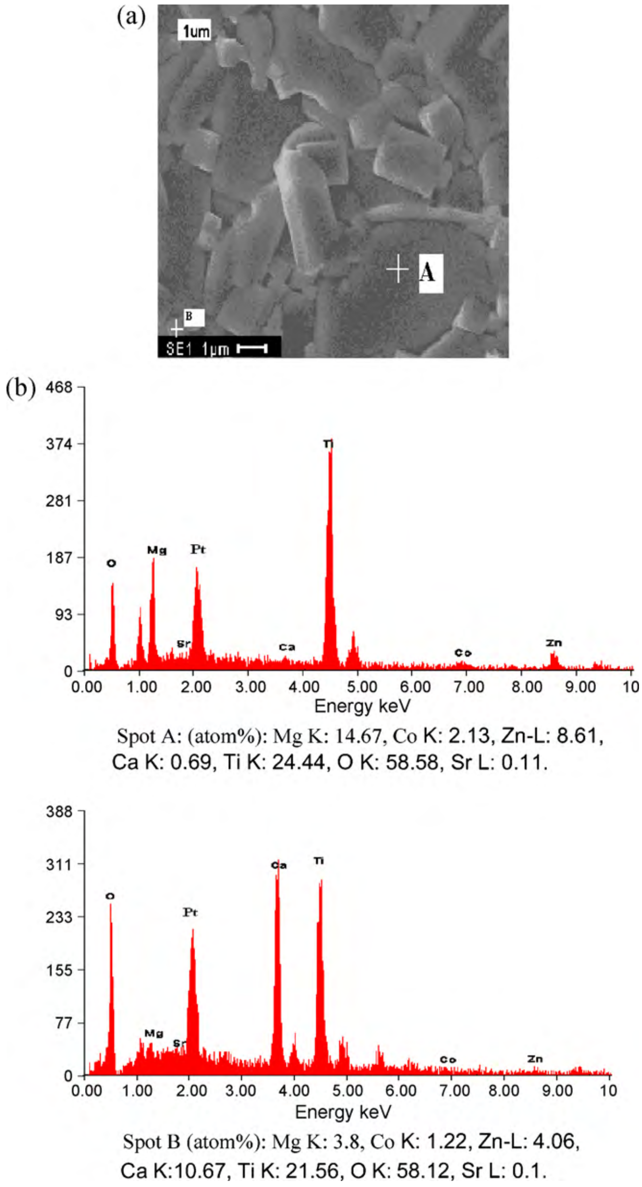


Fig. 2. SEM micrographs of $0.95(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.05Ca_{0.8}Sr_{0.2}TiO_3$ ceramics sintered at (a) 1100, (b) 1125, (c) 1150, (d) 1175, and (e) 1200 °C for 4 h.

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 $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sr_{0.2}TiO_3$ 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 90,000 GHz was obtained for $0.95(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.05Ca_{0.8}Sr_{0.2}TiO_3$ ceramic at 1150 °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 controlling dielectric loss, as has been shown for other microwave dielectric materials.

Fig. 7 illustrates the τ_f values of the $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sr_{0.2}TiO_3$ ceramic 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 $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}$ and $Ca_{0.8}Sr_{0.2}TiO_3$ are −65 and 990 ppm/°C, respectively, increasing $Ca_{0.8}Sr_{0.2}TiO_3$ content makes the τ_f value more positive. This implies that a zero τ_f value can be achieved by tuning the amount of $Ca_{0.8}Sr_{0.2}TiO_3$ content. In fact, with $x = 0.95$, a zero τ_f value was achieved for the $0.95(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}$–$0.05Ca_{0.8}Sr_{0.2}TiO_3$ ceramic system sintered at 1150 °C for 4 h.



Spot A: (atom%): Mg K: 14.67, Co K: 2.13, Zn-L: 8.61, Ca K: 0.69, Ti K: 24.44, O K: 58.58, Sr L: 0.11.

Spot B (atom%): Mg K: 3.8, Co K: 1.22, Zn-L: 4.06, Ca K:10.67, Ti K: 21.56, O K: 58.12, Sr L: 0.1.

Fig. 3. (a) The marks of SEM for the $0.95(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.05Ca_{0.8}Sr_{0.2}TiO_3$ ceramics sinter at 1150 °C and (b) EDX data of $0.95(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.05Ca_{0.8}Sr_{0.2}TiO_3$ ceramics for spots A–B.

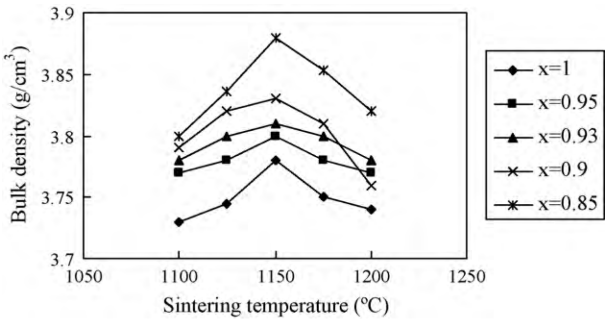


Fig. 4. Bulk density of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sr_{0.2}TiO_3$ ceramics as a function of the sintering temperature.

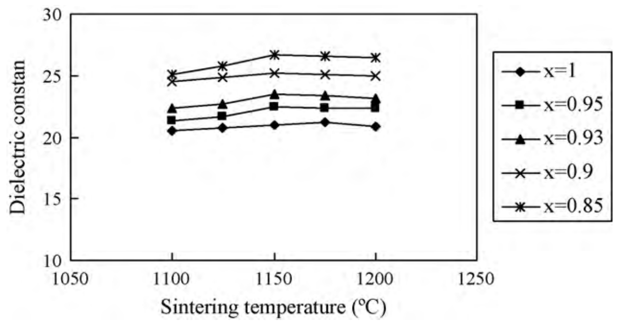


Fig. 5. Dielectric constants curves of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sr_{0.2}TiO_3$ ceramics at different sintering temperatures for 4 h.

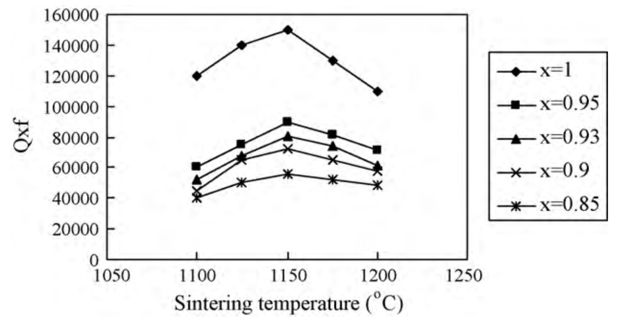


Fig. 6. $Q \times f$ and τ_f values of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sr_{0.2}TiO_3$ ceramics as a function of the sintering temperature.

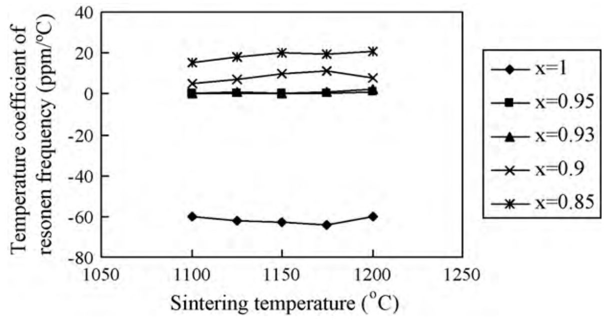


Fig. 7. τ_f values of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sr_{0.2}TiO_3$ system sintering at different temperatures for 4 h.

Table 1
Microwave dielectric properties of the $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sr_{0.2}TiO_3$ ceramics system sintered at 1150 °C for 4 h.

x value	Bulk density (g/cm^3)	ε_r	$Q \times f$ (GHz)	τ_f (ppm/°C)
1	3.78	20.95	140,000	−63
0.95	3.8	22.5	90,000	0
0.93	3.81	23.5	80,000	0.1
0.9	3.83	25.2	72,000	10
0.85	3.88	26.7	56,000	21

Table 1 shows the microwave dielectric properties of the $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sr_{0.2}TiO_3$ ceramic system sintered at 1150 °C for 4 h. When the $(1-x)$ value increased from 0.05 to 0.15, the τ_f values of the $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sr_{0.2}TiO_3$ ceramic system changed from 0 to 21 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 $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sr_{0.2}TiO_3$ ceramic system. With $x = 0.95$, the $0.95(Mg_{0.7}Zn_{0.3})_{0.95}$

$Co_{0.05}TiO_3$–$0.05Ca_{0.8}Sr_{0.2}TiO_3$ ceramic system shows good temperature stability with $\tau_f \sim 0$ ppm/°C. However, when the $Ca_{0.8}Sr_{0.2}TiO_3$ content was increased, the $Q \times f$ value decreased because the $Ca_{0.8}Sr_{0.2}TiO_3$ ceramic has a low $Q \times f$ value of 9000 GHz.

4. Conclusions

The dielectric properties of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sr_{0.2}TiO_3$ ceramic were investigated. $0.95(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.05Ca_{0.8}Sr_{0.2}TiO_3$ 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 $Ca_{0.8}Sr_{0.2}TiO_3$. 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 $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$(1-x)Ca_{0.8}Sr_{0.2}TiO_3$ 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 $Ca_{0.8}Sr_{0.2}TiO_3$. At 1150 °C, the $0.95(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$–$0.05Ca_{0.8}Sr_{0.2}TiO_3$ ceramic has been developed, exhibiting excellent microwave dielectric properties: $\varepsilon_r \sim 22.5$, $Q \times f \sim 90{,}000$ GHz (at 9 GHz), and $\tau_f \sim 0$ ppm/°C, which make it a suitable candidate material with a relatively low sintering temperature for ISM band components and GPS antennas.

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