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Low-loss microwave dielectrics in the $Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$(Ca_{0.8}Sr_{0.2})TiO_3$ ceramic system

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ABSTRACT

The microwave dielectric properties of the $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ ceramic system prepared by mixed oxide route have been investigated. The crystal structures and the microstructures of the ceramics were characterized by means of X-ray and SEM. The microwave dielectric properties are strongly related to the density and matrix of the specimen. Combination of $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ (spinel-structured) and $(Ca_{0.8}Sr_{0.2})TiO_3$ (perovskite-structured) forms a two-phase system and leads to a near-zero τ_f. With increasing x, the microwave $Q \times f$ decreased and ε_r increased. A new microwave dielectric material $0.91Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$0.09(Ca_{0.8}Sr_{0.2})TiO_3$, possessing excellent microwave dielectric properties with a dielectric constant (ε_r) of 18.32, a $Q \times f$ of 109,200 GHz (where f = 9.5 GHz, is the resonant frequency) and a τ_f value ∼–0.5 ppm/°C at 1270 °C for 4 h, is proposed as a suitable candidate material for microwave applications requiring low dielectric loss.

1. Introduction

The rapid growth of recent wireless communication systems led to an increasing demand for small-scale high-frequency resonators, filters and antennas capable of operating in the GHz range [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 [3–6]. At the same time, in order to work with high efficiency and stability, many researches have been focusing on developing new dielectric materials with a high quality factor ($Q \times f$) and a near-zero temperature coefficient of resonant frequency (τ_f) for use as dielectric resonator and microwave device substrate [7–9]. For instance, low-loss dielectrics with different dielectric constants have become most popular materials used for today's GPS patch antennas [10].

Many experiments have also been conducted to study the preparation and properties of Mg–Ti-based ceramics [11–13]. They have a spinel-structured, belonging to the cubic space group *Fd*-3*m* (2 2 7). Among them, Mg_2TiO_4, having a spinel-structured, belonging to the cubic space group *Fd*-3*m* (2 2 7), possesses a high dielectric constant $\varepsilon_r \sim 14$, a high $Q \times f$ value ∼150,000 GHz (at 10 GHz) and a negative τ_f value −50 ppm/°C [13]. Compounds such as $SrTiO_3$, $CaTiO_3$ and $(Ca_{0.8}Sr_{0.2})TiO_3$ have been individually employed as an effective τ_f compensator to materials having positive τ_f, such as $MgTiO_3$, Mg_2TiO_4, $La(Zn_{1/2}Ti_{1/2})O_3$ and $Ca(Mg_{1/3}Ta_{2/3})$ [9,13–16]. In our previous report, $0.91Mg_2TiO_4$–$0.09(Ca_{0.8}Sr_{0.2})TiO_3$ possessed a fine combination of dielectric properties ($\varepsilon_r \sim 18.3$, $Q \times f$ value ∼90,500 GHz, and $\tau_f \sim 0$ ppm/°C) [17]. Still, a higher $Q \times f$ is craved for high-frequency applications. Since the ionic radius of Sn^{4+} (0.69 Å) is similar to that of Ti^{4+} (0.605 Å) [18], Ti^{4+} ions can be substituted by Sn^{4+} ions to form $Mg_2(Ti,Sn)O_4$ compositions. With the partial replacement of Ti by Sn, the $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics, having a spinel-structure, was investigated to possess excellent dielectric properties with an ε_r value ∼15.57, a $Q \times f$ value ∼317,500 GHz (at 10.8 GHz) and a τ_f value ∼−45.1 ppm/°C [19]. However, the $Mg_2(Ti_{0.95}Sn_{0.05})TiO_4$ ceramics have a negative τ_f value, which is not suitable for practical use.

Since combining two dielectrics to balance the temperature coefficient of resonant frequency is a common method for high $Q \times f$ ceramics and has been shown for many other dielectrics [20], perovskite-structured $(Ca_{0.8}Sr_{0.2})TiO_3$ ($\varepsilon_r \sim 181$, $Q \times f$ value ∼8300 GHz, $\tau_f \sim 991$ ppm/°C) [21] was added to $Mg_2(Ti_{0.95}Sn_{0.05})TiO_4$ as a ceramic system $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})TiO_4$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ to achieve not only a near-zero τ_f, but also a higher $Q \times f$ compared to that of $0.91Mg_2TiO_4$–$0.09(Ca_{0.8}Sr_{0.2})TiO_3$. The dielectric properties at microwave frequencies of the sintered ceramics were characterized and discussed in terms of the densification and the compositional ratio of the specimens. In addition, the X-ray diffraction (XRD) patterning and scanning electron microscopy (SEM) analysis were also employed to study the crystal structures and microstructures of the ceramics.

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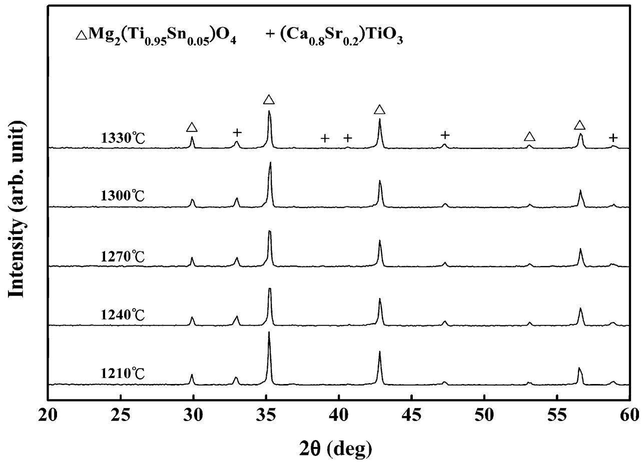


Fig. 1. X-ray diffraction patterns of $0.91Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$0.09(Ca_{0.8}Sr_{0.2})TiO_3$ ceramics sintered at different temperatures for 4 h.

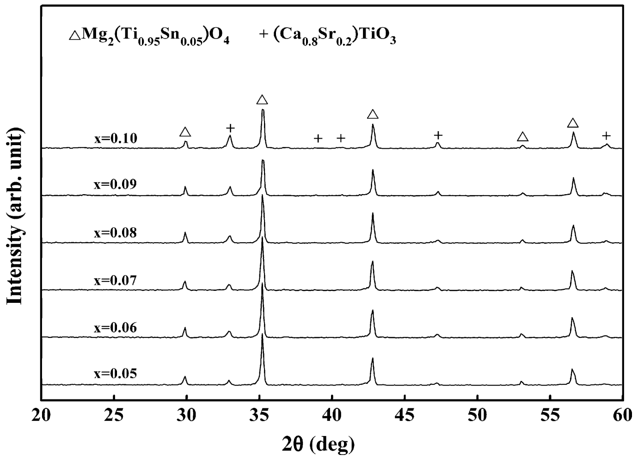


Fig. 2. X-ray diffraction patterns of $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ ceramic system sintered at 1270 °C for 4 h with different x values.

2. Experimental procedure

The starting materials were high-purity oxide powders (>99.9%): MgO, SnO_2, $CaCO_3$, $SrCO_3$ and TiO_2. The powders were separately prepared according to the desired stoichiometry $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ and $(Ca_{0.8}Sr_{0.2})TiO_3$, and ground in distilled water for 24 h in a ball mill with agate balls. The prepared powders were dried and calcined at 1100 °C for 24 h in air. After calcinations, the calcined powders were mixed according to the molar fraction $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ (x = 0.05–0.1) and then re-milled for 24 h. The fine powder with 3 wt% of a 10% solution of PVA as a binder (PVA 500, Showa, Japan) was pressed into pellets with dimensions of 11 mm in diameter and 5 mm in thickness under the pressure of 2000 kg/cm^2. These pellets were sintered at temperatures of 1210–1330 °C for 4 h in air. The heating rate and the cooling rate were both set at 10 °C/min.

The crystalline phases of the sintered ceramics were identified by XRD using Cu $K\alpha$ (λ = 0.15406 nm) radiation with a Siemens D5000 diffractometer operated at 40 kV and 40 mA. The microstructural observations and analysis of sintered surface were performed using a scanning electron microscopy (SEM) and an energy dispersive X-ray spectrometer (EDX). The apparent densities 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 constant (ε_r) and the quality factor values (Q) at microwave frequencies were measured using the Hakki-Coleman dielectric resonator method [22,23]. A system combining a HP8757D network analyzer (Palo Alto, CA) and a HP8350B sweep oscillator (Palo Alto, CA) was employed in the measurement. 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 from 20 to 80 °C.

3. Results and discussion

Fig. 1 shows the XRD patterns of $0.91Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$0.09(Ca_{0.8}Sr_{0.2})TiO_3$ (hereafter referred to as 91MTS–9CST) ceramics sintered at different temperatures for 4 h. The XRD patterns showed that peaks indicating the presence of $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ as the main crystalline phase, in association with $(Ca_{0.8}Sr_{0.2})TiO_3$ as a minor phase. The X-ray diffraction patterns of the 91MTS–9CST ceramics have not change significantly with sintering temperatures in the range 1210–1330 °C. Moreover, XRD patterns of $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ ceramic system sintered at 1270 °C for 4 h are shown in Fig. 2. With the increase in x $(Ca_{0.8}Sr_{0.2})TiO_3$ phase appeared, gradually enhanced, and a two-phase system was clearly observed.

The SEM micrographs of 91MTS–9CST ceramics sintered at different temperatures for 4 h are illustrated in Fig. 3. The 91MTS–9CST ceramics were not dense and the grain did not grow at 1210 °C. Porous microstructures were observed at 1210 °C. The grains, however, started to grow at 1240 °C and significant increase in the grain size was observed at 1300 °C. However, abnormal grain growth was also observed at 1330 °C, which might degrade the microwave dielectric properties of the ceramics. Energy dispersive X-ray (EDX) analysis was used in combination with scanning electron microscopy to distinguish every grain for 91MTS–9CST ceramics sintered at 1270 °C, as shown in Fig. 3(c). The EDX data of corresponding spots A–D are shown in Table 1. The grain morphology of well-developed 91MTS–9CST ceramics could be grouped into two types: large grains (spots A and B) were $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ and small cubic-shape grains (spots C and D) were $(Ca_{0.8}Sr_{0.2})TiO_3$. It revealed the EDX evidences were in agreement with the XRD results that obtained from 91MTS–9CST ceramics.

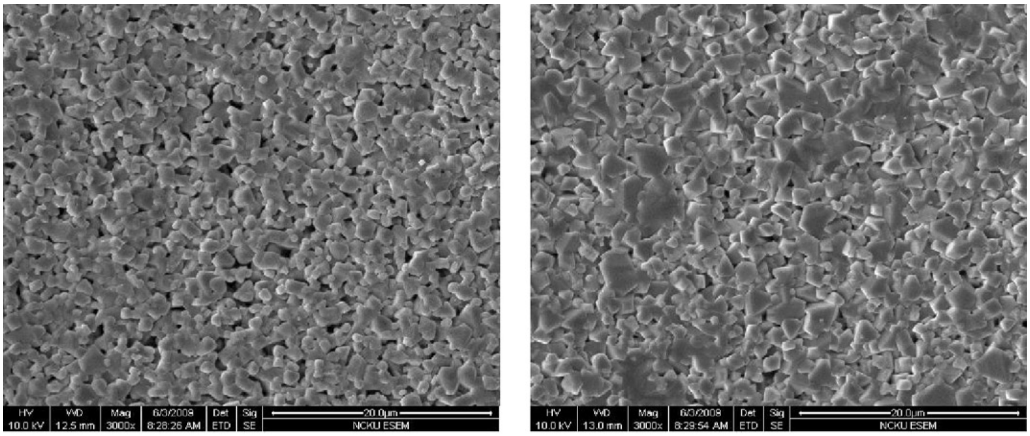
Fig. 4 shows the apparent densities of $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ ceramic system sintered at different temperatures for 4 h. With increasing sintering temperature, the apparent density of 91MTS–9CST was found to increase to a maximum value of 3.54 g/cm^3 at 1270 °C and thereafter decreased. Moreover, the degradation of apparent density at 1330 °C was owing to the abnormal grain growth as shown in Fig. 3.

Fig. 5 shows the dielectric constants of $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ ceramic system sintered at different temperatures for 4 h. Variation of ε_r value was consistent with that of density. The dielectric constant of 91MTS–9CST increased with increasing sintering temperature. After reaching its maximum at 1270 °C, it decreased. A maximum ε_r value of 18.32 was obtained for 91MTS–9CST ceramics sintered at 1270 °C for 4 h. It indicated higher sintering temperature does not necessarily lead the specimen to a higher dielectric constant.

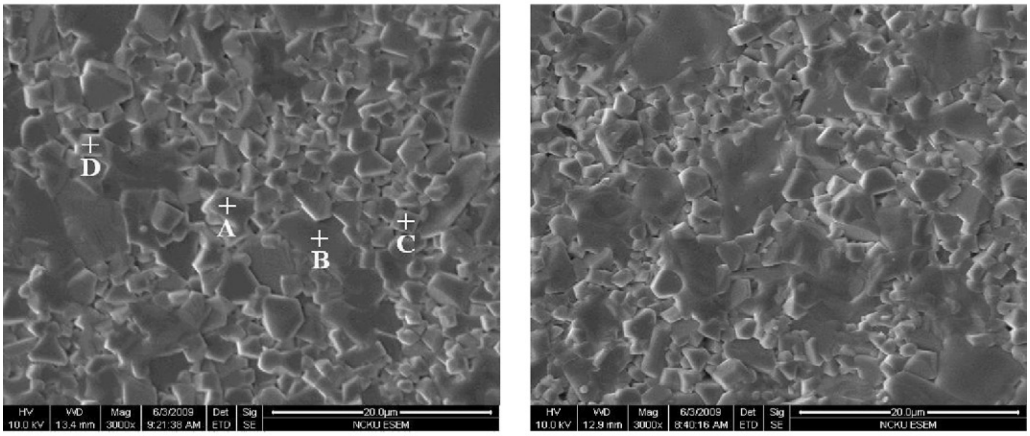
The $Q \times f$ values of $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ ceramic system sintered at different temperatures for 4 h is demonstrated in Fig. 6. By increasing the sintering temperature, the $Q \times f$ value of 91MTS–9CST was found to increase to a maximum value and decreased thereafter. It showed a similar trend with that of density because densification of the ceramics plays an important role in controlling the dielectric loss, and same phenomenon has been shown for other microwave dielectric materials. A maximum

Table 1
The EDX data of the spots A–D shown in Fig. 3(c).

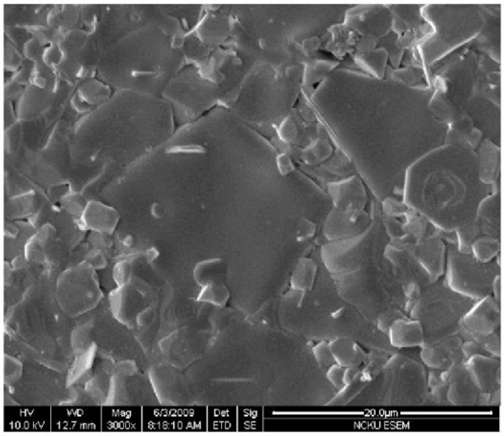
Spots	Atom (%)					
	Mg K	Sn L	Ca K	Sr L	Ti K	O K
A	30.85	0.82	0	0	12.62	55.71
B	29.02	0.93	0	0	14.27	55.78
C	0	0	12.11	3.49	14.40	70.00
D	0	0	13.38	3.50	16.04	67.08



(a) 1210°C (b) 1240°C



(c) 1270°C (d) 1300°C



(e) 1330°C

Fig. 3. SEM micrographs of $0.91Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$0.09(Ca_{0.8}Sr_{0.2})TiO_3$ ceramics sintered at (a) 1210 °C, (b) 1240 °C, (c) 1270 °C, (d) 1300 °C and (e) 1330 °C for 4 h.

$Q \times f$ value of 109,200 GHz (at 9.5 GHz), showing a 20.7% increase compared with that of $0.91Mg_2TiO_4$–$0.09(Ca_{0.8}Sr_{0.2})TiO_3$ ceramics [17], is obtained for the 91MTS–9CST ceramics sintered at 1270 °C for 4 h. The degradation of $Q \times f$ value was attributed to the abnormal grain growth resulted in a reduction of density as observed in Figs. 3 and 4. The microwave dielectric loss is caused not only by the lattice vibrational modes, but also by the pores, the second phases, the impurities, or the lattice defect [24–26]. In this case, the dielectric loss of the 91MTS–9CST ceramics is likely dominated by the density.

Fig. 7 illustrates the temperature coefficients of resonant frequency (τ_f) of $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ ceramic system sintered at 1210–1330 °C for 4 h with different x values. The temperature coefficient of resonant frequency is well known to be governed by the composition, the additives, and the second phase of the materials. Increasing $(Ca_{0.8}Sr_{0.2})TiO_3$ content would make the τ_f value of the specimen more positive because the τ_f values of $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ [19] and $(Ca_{0.8}Sr_{0.2})TiO_3$ [21] are −45.1 and 991 ppm/°C, respectively. It also implies that a zero τ_f can be achieved by increasing the amount of $(Ca_{0.8}Sr_{0.2})TiO_3$ content. The

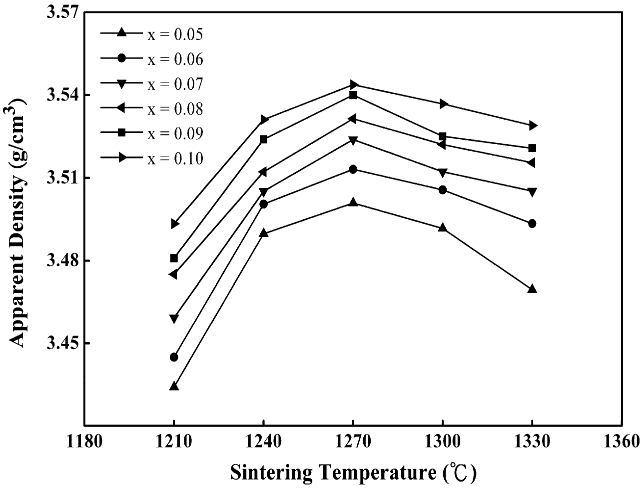


Fig. 4. Apparent density of $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ ceramic system as a function of its sintering temperature.

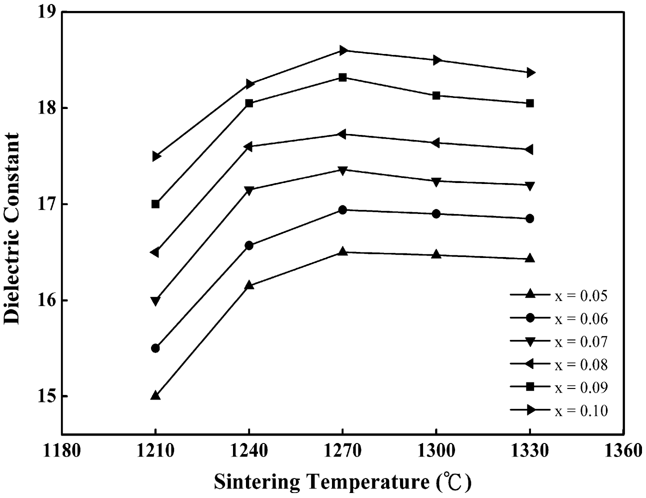


Fig. 5. Dielectric constant of $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ ceramic system as a function of its sintering temperature.

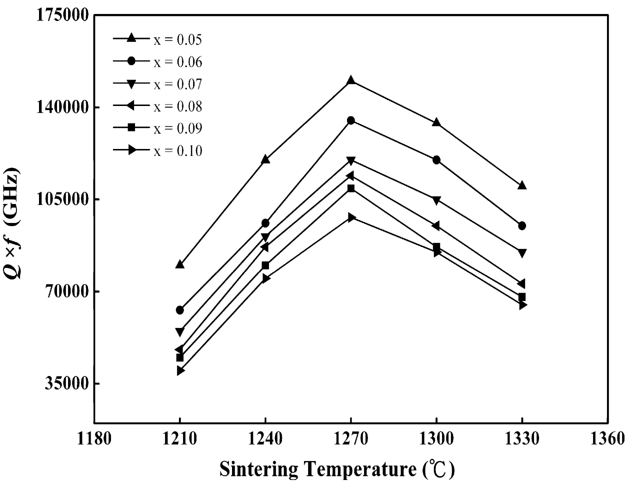


Fig. 6. $Q \times f$ value of $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ ceramic system as a function of its sintering temperature.

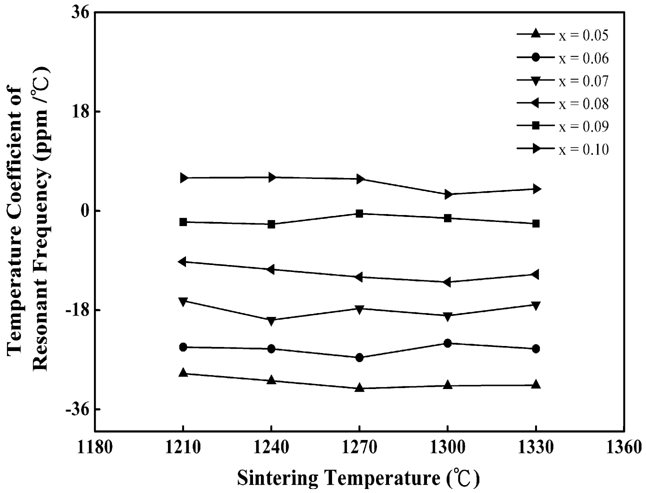


Fig. 7. τ_f value of $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ ceramic system as a function of its sintering temperature.

τ_f value of −0.5 ppm/°C can be obtained for 91MTS–9CST ceramics sintered at 1270 °C for 4 h.

4. Conclusion

$(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ ceramic system showed mixed phases of $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ as the main phase in association with the minor phase $(Ca_{0.8}Sr_{0.2})TiO_3$. The microwave dielectric properties are strongly related to the density and the matrix of the specimen. With $x = 0.09$, a near-zero τ_f value can be achieved for $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ ceramic system. A dielectric constant (ε_r) value of 18.32, a $Q \times f$ value of 109,200 GHz (measured at 9.5 GHz) and a τ_f value of −0.5 ppm/°C were obtained for 91MTS–9CST ceramics sintered at 1270 °C for 4 h. Obviously, 91MTS–9CST is suitable for applications as microwave dielectric resonators and filters because of its excellent combination of microwave dielectric properties.

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