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Characterization and dielectric behavior of a new dielectric ceramics $MgTiO_3$–$Ca_{0.8}Sr_{0.2}TiO_3$ at microwave frequencies

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ABSTRACT

The crystal structures, phase compositions and the microwave dielectric properties of the $(1-x)MgTiO_3$–$xCa_{0.8}Sr_{0.2}TiO_3$ composites prepared by the conventional solid state route have been investigated. The formation of solid solution is confirmed by the XRD patterns. A rapid grain growth is observed at temperatures higher than 1300 °C, which would lead to a decrease in the density and $Q \times f$ of the ceramics. The temperature coefficient of resonant frequency (τ_f) increases with increasing $Ca_{0.8}Sr_{0.2}TiO_3$ content and tunes through near zero at $x = 0.06$. Specimen using $0.94MgTiO_3$–$0.06Ca_{0.8}Sr_{0.2}TiO_3$ possesses an excellent combination of microwave dielectric properties: $\varepsilon_r \sim 21.9$, $Q \times f \sim 128{,}000$ GHz and $\tau_f \sim 0.7$ ppm/°C. It is proposed as a suitable candidate material for small-sized GPS patch antennas.

1. Introduction

The growing importance of ceramic dielectrics for applications as microwave oscillators, filters, etc., has led to great advances in the material research and development of dielectric ceramic systems [1]. Miniaturization of microwave circuits using low loss and temperature stable dielectric ceramic resonators has spurred the wireless communication industry enormously.

Basically, a dielectric resonator is a ceramic compact with high dielectric constant ($\varepsilon_r > 25$), low dielectric loss or high quality factor ($Q > 2000$) and good temperature stability (near-zero temperature coefficient of resonant frequency, τ_f) at microwave frequencies [2–13].

Most of the ceramic dielectrics developed so far for microwave applications are composed of mixed phases consisting of different compounds in the multi-component systems. In order to meet the requirements for use in microwave resonators and filters, dielectric materials must satisfy stringent physical properties. These requirements greatly restrict the number of materials that can be considered for use in actual devices. With this objective, many dielectric ceramic compositions such as $BaTi_4O_9/BaTi_9O_{20}$ [14], $(Zn,Sn)TiO_4$ [15], $Ba(Mg_{1/3}Ta_{2/3})O_3$ [16,17], $Ba(Zn_{1/3},Ta_{2/3})O_3$ [18], etc., have been developed and successfully integrated with microwave circuits.

Two conventional approaches are usually employed in the development of excellent dielectric ceramics; one is to create a new dielectric ceramic material and the other is to combine more than two materials with characteristic compensation. The most popular method is to mix two or more compositions with different dielectric properties. In other words, to adjust the temperature coefficient (τ_f) to zero, two or more compounds having negative and positive τ_f values are used to form a solid solution or mixed phases [19].

$MgTiO_3$-based ceramics has been widely applied to dielectrics in resonators, filters and antennas for communication, radar, and global positioning systems operated at microwave frequencies. $MgTiO_3$–$CaTiO_3$ (MCT hereafter) ceramics have an ilmenite-type structure, which belongs to the trigonal space group $R\bar{3}$. In the microwave frequency range, $MgTiO_3$ ceramics show good dielectric properties: dielectric constant (ε_r) ~17, quality factor ($Q \times f$ value) ~160,000 (GHz), and temperature coefficients of resonant frequency (τ_f) approximately −51 ppm/°C [20]. Instead of CaTiO, $Ca_{0.8}Sr_{0.2}TiO_3$ ceramics having much higher dielectric properties of $\varepsilon_r \sim 181$, $Q \times f$ value ~8300 (GHz) and a large positive τ_f value ~991 ppm/°C [21] than that of $CaTiO_3$ (Table 1) was chosen as a τ_f compensator for $MgTiO_3$.

In this study, $Ca_{0.8}Sr_{0.2}TiO_3$ was added to $MgTiO_3$ to make a ceramic system of $(1-x)MgTiO_3$–$xCa_{0.8}Sr_{0.2}TiO_3$, which demonstrated an effective compensation of its τ_f value. The resultant microwave dielectric properties were analyzed using densification, X-ray diffraction patterns, and the microstructures of the ceramics. The correlation between the microstructure and the $Q \times f$ value was also investigated.

2. Experimental procedures

The raw materials MgO and TiO_2 were mixed according to the composition of $MgTiO_3$ and the purity of these powders was higher than 99.9%. They were

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Table 1
Microwave dielectric properties of dielectric ceramics.

Phase	ε_r	$Q \times f$ (GHz)	τ_f (ppm/°C)
$MgTiO_3$	17	160,000	−55
$CaTiO_3$	170	3600	800
$SrTiO_3$	200	4200	1700
$Ca_{0.8}Sr_{0.2}TiO_3$	181	8300	991

Table 2
Microwave dielectric properties of $(1-x)MgTiO_3$–$xCa_{0.8}Sr_{0.2}TiO_3$ ceramic system sintered at 1350 °C for 4 h.

x value	Density (g/cm^3)	ε_r	$Q \times f$	τ_f (ppm/°C)
0.02	3.65	19.8	150,000	−35.7
0.04	3.67	20.5	142,000	−20
0.05	3.69	21.1	135,000	−9.8
0.06	3.7	21.9	128,000	0.7
0.08	3.73	23.6	115,000	29
0.1	3.77	25.1	107,000	65.5

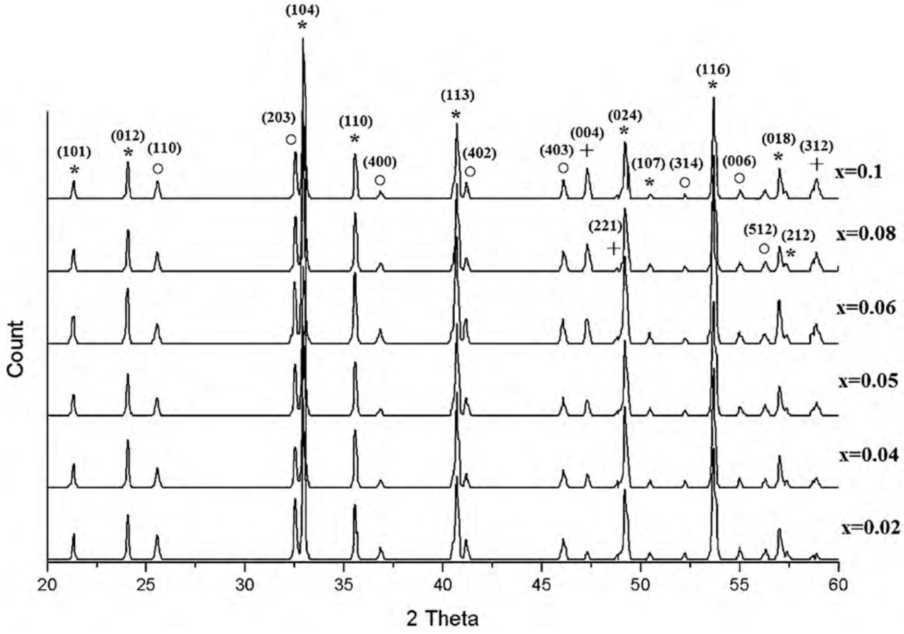


Fig. 1. X-ray diffraction patterns of $(1-x)MgTiO_3$–$xCa_{0.8}Sr_{0.2}TiO_3$ ceramics as a function of the x value, sintered at 1275 °C/4 h.

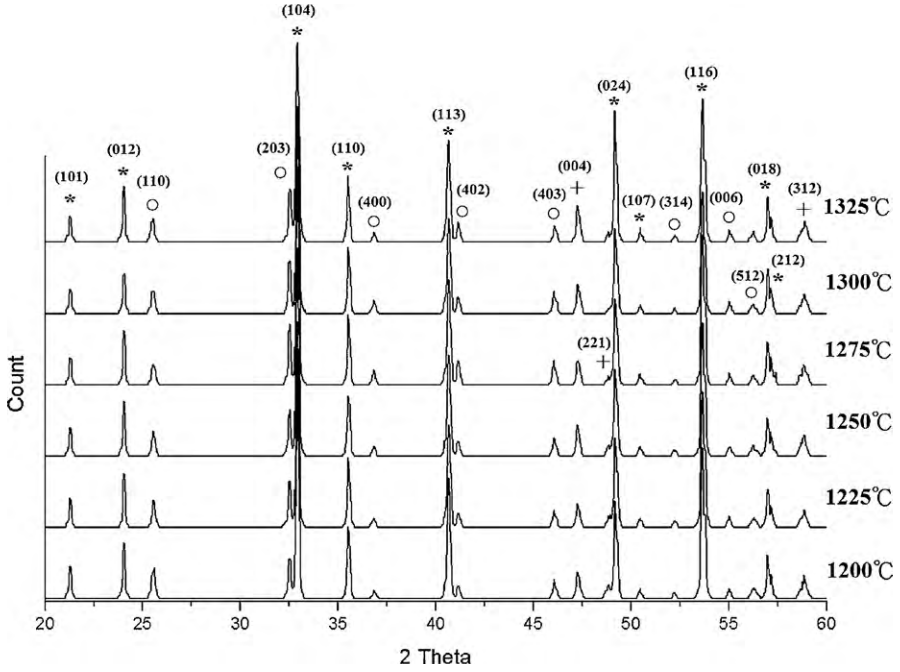


Fig. 2. X-ray diffraction patterns of $0.94MgTiO_3$–$0.06Ca_{0.8}Sr_{0.2}TiO_3$ ceramics sintered at various temperatures for 4 h.

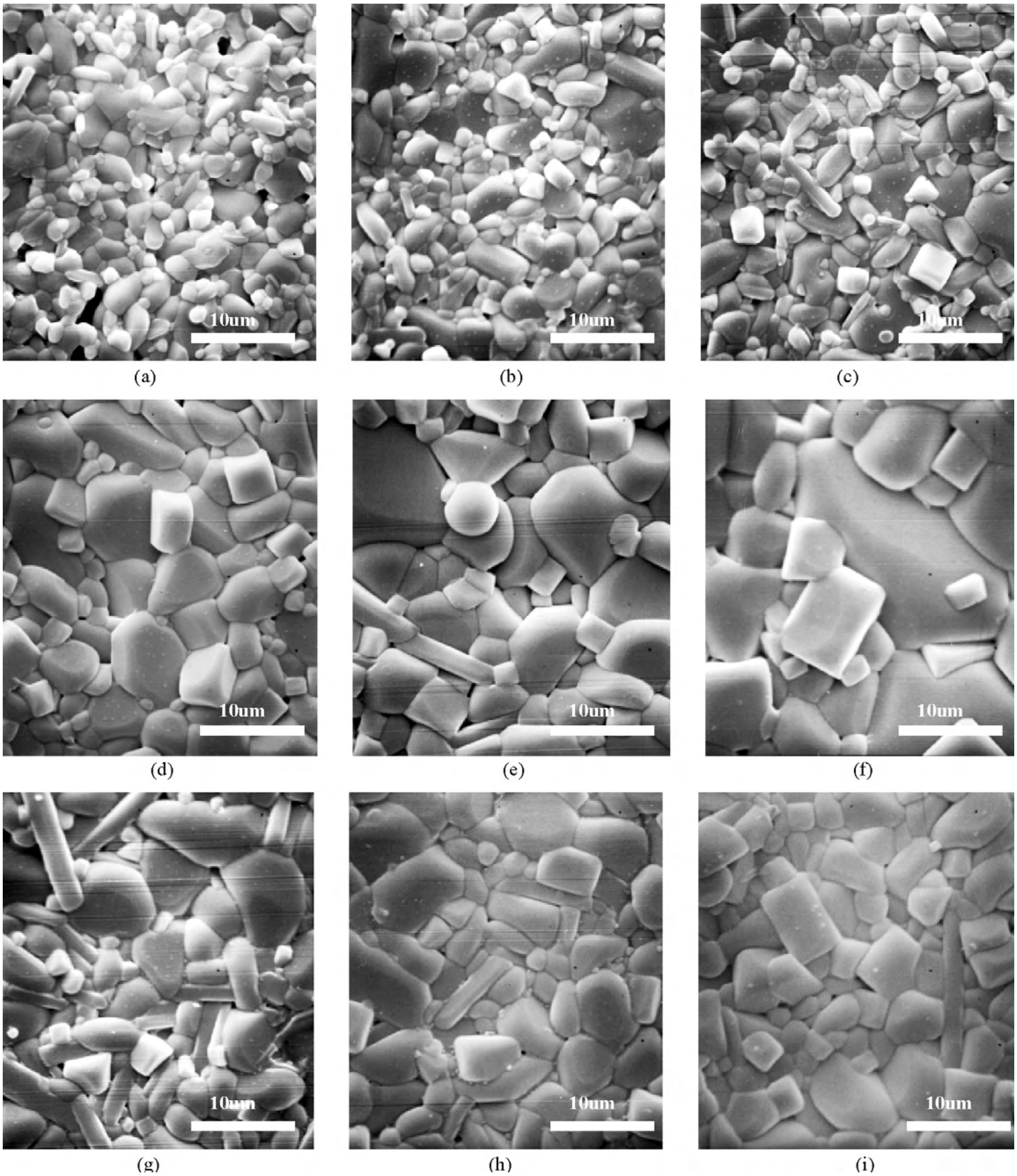


Fig. 3. SEM micrographs of $0.94MgTiO_3$–$0.06Ca_{0.8}Sr_{0.2}TiO_3$ ceramics sintered at (a) 1200 °C, (b) 1225 °C, (c) 1250 °C, (d) 1275 °C, (e) 1300 °C and (f) 1325 °C for 4 h.

milled with ZrO_2 balls in distilled water for 24 h, then dried and calcined in air at 1100 °C for 4 h. $CaCO_3$, $SrCO_3$ and TiO_2 were mixed aside according to the stoichiometry of $Ca_{0.8}Sr_{0.2}TiO_3$. They were milled with ZrO_2 balls in distilled water for 24 h, then dried and calcined in air at 1100 °C for 4 h. After that, the two kinds of calcined powders were mixed together according to the composition of $(1-x)MgTiO_3$–$xCa_{0.8}Sr_{0.2}TiO_3$ (x = 0.02, 0.04, 0.05, 0.06, 0.08 and 0.1), milled again for 24 h and dried. Then they were sieved with a 100-mesh screen and pressed homogeneously into pellets at 75 MPa with dimensions of 11 mm in diameter and 5 mm in thickness. The pellets were sintered in air at 1200–1325 °C for 4 h at a heating rate of 10 °C/min.

The densities of the sintered ceramics were measured using the Archimedes method. The crystalline phases of the sintered ceramics were identified by XRD using Cu Kα (0.15406 nm) radiation with a Siemens D5000 diffractometer (Siemens, Munich, Germany) operated at 40 kV and 40 mA. The surface microstructure was observed with Scanning Electronic Microscope (SEM) and Energy Dispersive Spectroscopy (EDS). The dielectric constants and the Q values were measured by employing the Hakki and Coleman method [22,23]. The apparatus consisted of parallel conducting brass plates and coaxial probes connected to a HP8757B S-parameter network analyzer and an HP8350B sweep oscillator. The temperature coefficient of resonant frequency (τ_f) was measured with the test set which was placed over a thermostat in the temperature range from 25 to 80 °C. The τ_f value was calculated using the equation $sf = (f_{85} - f_{25})/f_{25}$ (60 °C), where f_{85} and f_{25} are the resonant frequency of the samples at 85 and 25 °C, respectively.

3. Results and discussion

Table 2 demonstrates the microwave dielectric properties of $(1-x)MgTiO_3$–$xCa_{0.8}Sr_{0.2}TiO_3$ ceramics sintered at 1275 °C for 4 h.

Table 3
The lattice parameter of $(1-x)MgTiO_3$–$xCa_{0.8}Sr_{0.2}TiO_3$ ceramic sintered at 1275 °C/4 h.

x value	a	c
0.02	0.50568 ± 0.00009	1.3928 ± 0.0003
0.04	0.50546 ± 0.00029	1.39013 ± 0.00095
0.05	0.50481 ± 0.00007	1.39206 ± 0.00024
0.06	0.50494 ± 0.00029	1.38833 ± 0.00094
0.08	0.50491 ± 0.00029	1.38825 ± 0.00094
0.1	0.50546 ± 0.00029	1.39013 ± 0.00095

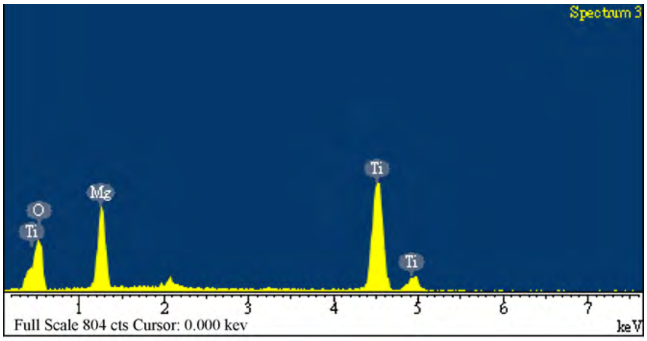
Significant variation in the dielectric properties can be observed due to a different compositional ratio. It was mainly a result from a difference in the dielectric properties for each composition. Since the specimen using $0.94MgTiO_3$–$0.06Ca_{0.8}Sr_{0.2}TiO_3$ ceramic shows a good temperature stability with $\tau_f \sim 0.7$ ppm/°C a more comprehensive and closer investigation on the microwave dielectric properties of $0.94MgTiO_3$–$0.06Ca_{0.8}Sr_{0.2}TiO_3$ ceramic was then conducted.

X-ray diffraction patterns of $(1-x)MgTiO_3$–$xCa_{0.8}Sr_{0.2}TiO_3$ ceramics sintered at 1275 °C/4 h for values of x ranging from 0.02 to 0.1 are shown in Fig. 1. $(1-x)MgTiO_3$–$xCa_{0.8}Sr_{0.2}TiO_3$ ceramics showed a mixture of a main phase $MgTiO_3$ and a minor phase $Ca_{0.8}Sr_{0.2}TiO_3$. The formation of $MgTiO_3$ (ilmenite) and $Ca_{0.8}Sr_{0.2}TiO_3$ (perovskite) was due to the structure and ionic size differences between Ca^{2+} (0.1 nm) and Mg^{2+} (0.046 nm) [24]. Moreover, a second $MgTi_2O_5$ ($\varepsilon_r \sim 17.4$, $Q \times f \sim 47{,}000$ GHz, $\tau_f \sim -66$ ppm/°C) was also detected, which would lead to a degradation in dielectric properties. It was attributed to that $MgTi_2O_5$ is usually formed as an intermediate phase and is difficult to eliminate completely from the sample when MgO and TiO_2 reacts in a 1:1 molar ratio [25,26]. The relative intensity of $MgTi_2O_5$ decreased with increasing x owing a decrease in the compositional content (Mg, Ti). Similar XRD patterns were obtained for specimen at different temperatures (Fig. 2) except that second phase $MgTi_2O_5$ was enhanced at higher temperatures. It showed an increase in its intensity as the sintering temperature increased.

The lattice parameters of $(1-x)MgTiO_3$–$xCa_{0.8}Sr_{0.2}TiO_3$ ceramics at 1275 °C/4 h were also measured in this study. It was found that $MgTiO_3$ has a hexagonal structure with the following lattice parameters: $a = b = 0.5054$ nm, $c = 1.3898$ nm (ICDD-PDF#00-006-0494). When $Ca_{0.8}Sr_{0.2}TiO_3$ was added to $MgTiO_3$ to form a ceramic system of $(1-x)MgTiO_3$–$xCa_{0.8}Sr_{0.2}TiO_3$, the lattice parameters of $MgTiO_3$ did not change with $Ca_{0.8}Sr_{0.2}TiO_3$ content as shown in Table 3. Furthermore, the formation of mixed phases in the $(1-x)MgTiO_3$–$xCa_{0.8}Sr_{0.2}TiO_3$ ceramics system was due to structural differences and because the average ionic radii of Ca^{2+} (0.1 nm) and Sr^{2+} (0.144 nm) were larger than these of Mg^{2+} (0.046 nm). This confirms the existence of a two-phase ceramic system of $(1-x)MgTiO_3$–$xCa_{0.8}Sr_{0.2}TiO_3$, with $MgTiO_3$ as the main crystalline phase and $Ca_{0.8}Sr_{0.2}TiO_3$ as the minor phase. These results are in agreement with XRD patterns.

Fig. 3 shows the surface microstructural photographs of the specimens using $0.94MgTiO_3$–$0.06Ca_{0.8}Sr_{0.2}TiO_3$ ceramics sintering at different temperatures for 4 h. As illustrated, the result indicates that the specimen does not appear dense and the grain is not grown at 1200 °C. In addition, the grain size increases as the sintering temperature increases. The pores are almost eliminated for specimen sintered at 1275 °C, and a noticeable grain growth and a relatively uniform surface morphology are observed at 1275 °C. However, rapid grain growth is monitored at temperatures 1300 and 1325 °C and some pores start to appear, which might degrade the microwave dielectric properties of the ceramics. The Energy Dispersive Spectroscopy (EDS) of the needle shape grains in Fig. 3 were identified as a second phase of $MgTi_2O_5$ (Mg:Ti = 1:2) as shown in Fig. 4, which could lead to the degradation in dielectric properties.

The apparent densities of the $(1-x)MgTiO_3$–$xCa_{0.8}Sr_{0.2}TiO_3$ ceramics system at various sintering temperatures as functions of the x value are shown in Fig. 5. The density of the specimens initially increased with increasing sintering temperature, attaining a maximum value at 1275 °C. This increase in the density can be attributed to the formation of dense microstructures. The density decreased when the sintering temperature exceeded 1300 °C. This decrease in the density could be related to inhomogeneous microstructure evolution. It was also affected by the composition and increased with increasing x value. This suggests that higher $Ca_{0.8}Sr_{0.2}TiO_3$ content would exhibit relatively higher densities in the ceramics, since $Ca_{0.8}Sr_{0.2}TiO_3$ ($D \sim 4.28$ g/cm^3) possesses a higher density than that of $MgTiO_3$ ($D \sim 3.89$ g/cm^3). At 1275 °C, the density of the $(1-x)MgTiO_3$–$xCa_{0.8}Sr_{0.2}TiO_3$ ceramics increased from 3.65 to 3.77 g/cm^3 as the x value increased from 0.02 to 0.1.



Atom(%)		
Mg	Ti	O
12.68	23.39	63.93

Fig. 4. The EDS results of needle-shaped grains illustrated in Fig. 3.

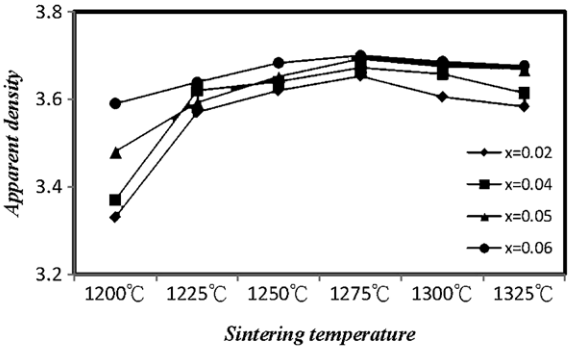


Fig. 5. Apparent density of $(1-x)MgTiO_3$–$xCa_{0.8}Sr_{0.2}TiO_3$ ceramics with different x values as a function of sintering temperature.

Fig. 6 shows the dielectric constants (ε_r) of $(1-x)MgTiO_3$–$xCa_{0.8}Sr_{0.2}TiO_3$ ceramics at various sintering temperatures as functions of the x value. The relationships between ε_r values and sintering temperatures reveal the same trend as that between densities and sintering temperatures, since higher density means lower porosity. The dielectric constant (ε_r) slightly increased with increasing sintering temperature. The increase in the dielectric constant (ε_r) is a result of higher density. Since $Ca_{0.8}Sr_{0.2}TiO_3$ possesses a much higher dielectric constant

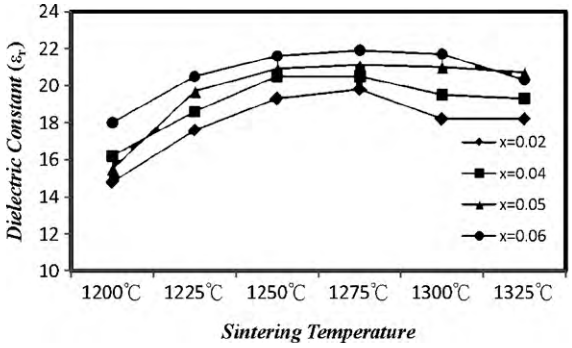


Fig. 6. Dielectric constant (ε_r) of $(1-x)MgTiO_3$–$xCa_{0.8}Sr_{0.2}TiO_3$ ceramics with different x values as a function of the sintering temperature.

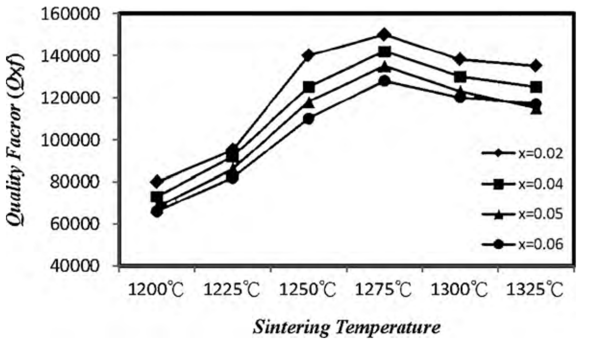


Fig. 7. $Q \times f$ values of $(1-x)$MgTiO$_3$–xCa$_{0.8}$Sr$_{0.2}$TiO$_3$ ceramics with different x values as a functions of sintering temperature.

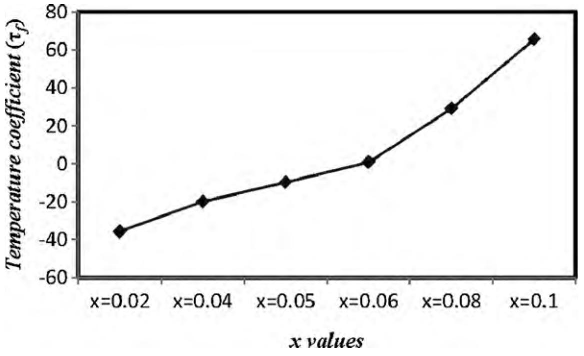


Fig. 8. τ_f value of $(1-x)$MgTiO$_3$–xCa$_{0.8}$Sr$_{0.2}$TiO$_3$ ceramics sintered at 1275 °C/4 h as a function of the x value.

than MgTiO$_3$ does ($\varepsilon_r = 181$ for Ca$_{0.8}$Sr$_{0.2}$TiO$_3$; ~17 for MgTiO$_3$), the dielectric constant (ε_r) of $(1-x)$MgTiO$_3$–xCa$_{0.8}$Sr$_{0.2}$TiO$_3$ ceramics increased as the x value increased. At 1275 °C, the dielectric constant (ε_r) of $(1-x)$MgTiO$_3$–xCa$_{0.8}$Sr$_{0.2}$TiO$_3$ ceramics increased from 19.8 to 25.1 as the x value increased from 0.02 to 0.1.

Fig. 7 shows the quality factor ($Q \times f$ value) of $(1-x)$MgTiO$_3$–xCa$_{0.8}$Sr$_{0.2}$TiO$_3$ ceramics with various x values as a function of sintering temperature. The $Q \times f$ value is an important index for applications of dielectric ceramics at microwave frequencies because a higher $Q \times f$ value means a lower dielectric loss for microwave devices. The microwave dielectric loss is mainly by the lattice vibrational modes, the pores, and the second phases [27]. The quality factor of MgTiO$_3$ ($Q \times f$ value ~ 160,000) is much higher than that of Ca$_{0.8}$Sr$_{0.2}$TiO$_3$ ($Q \times f$ value ~ 8300) and hence it is expected that the $Q \times f$ values will decrease as the amount of Ca$_{0.8}$Sr$_{0.2}$TiO$_3$ increases from 0.02 to 0.1. Fig. 7 shows that the quality factor of $(1-x)$MgTiO$_3$–xCa$_{0.8}$Sr$_{0.2}$TiO$_3$ ceramics decreases with the composition (x) as expected. The $Q \times f$ value increases when the sintering temperature increases from 1200 to 1275 °C. After reaching its maximum value at 1275 °C, the $Q \times f$ value decreased. The increase in $Q \times f$ value at low temperatures is due to the increase in density as well as the uniformity of grain growth, as shown in Fig. 3. At 1275 °C, the maximum $Q \times f$ value of 128,000 (GHz) was obtained for the 0.94MgTiO$_3$–0.06 Ca$_{0.8}$Sr$_{0.2}$TiO$_3$ ceramics. The degradation of $Q \times f$ value can be attributed to inhomogeneous grain growth which results in a reduction of density, as shown in Fig. 3. Relative density also plays an important role in controlling the dielectric loss, as has been shown in other microwave dielectric materials. The $Q \times f$ value of $(1-x)$MgTiO$_3$–xCa$_{0.8}$Sr$_{0.2}$TiO$_3$ ceramics is consistent with density variation, suggesting that dielectric loss of $(1-x)$MgTiO$_3$–xCa$_{0.8}$Sr$_{0.2}$TiO$_3$ ceramics is mainly controlled by the bulk density.

The temperature coefficients of resonant frequency (τ_f) of $(1-x)$MgTiO$_3$–xCa$_{0.8}$Sr$_{0.2}$TiO$_3$ ceramics sintered at 1275 °C/4 h as functions of the x value are shown in Fig. 8. The temperature coefficient of resonant frequency is related to the composition, the additives, and the second phase of the material. Due to the large positive τ_f value of Ca$_{0.8}$Sr$_{0.2}$TiO$_3$ ($\tau_f = 991$ ppm/°C), the τ_f values of $(1-x)$MgTiO$_3$–xCa$_{0.8}$Sr$_{0.2}$TiO$_3$ ceramics rapidly increases with increasing x value. The τ_f value is shifted from negative to positive as the x value increases from 0.02 to 0.1. This implies that $\tau_f = 0$ ppm/°C can be obtained by adjusting the amount of the Ca$_{0.8}$Sr$_{0.2}$TiO$_3$ additive.

4. Conclusions

Microwave dielectric properties of $(1-x)$MgTiO$_3$–xCa$_{0.8}$Sr$_{0.2}$TiO$_3$ ceramics were investigated. For $(1-x)$MgTiO$_3$–xCa$_{0.8}$Sr$_{0.2}$TiO$_3$ ceramics sintered at 1200–1325 °C for 4 h, as the amount of Ca$_{0.8}$Sr$_{0.2}$TiO$_3$ (x value) increased from 0.02 to 0.1, the dielectric constant increased from 19.8 to 25.1, the temperature coefficient of resonant frequency (τ_f) increased from −35.7 to 65.5 ppm/°C, and the $Q \times f$ value decreased from 150,000 (GHz) to 107,000 (GHz). At the composition of $x = 0.06$, the 0.94MgTiO$_3$–0.06Ca$_{0.8}$Sr$_{0.2}$TiO$_3$ ceramics sintered at 1275 °C/4 h have excellent microwave dielectric properties: a dielectric constant (ε_r) of 21.9, a $Q \times f$ value of 128,000 (GHz), and a τ_f value of 0.7 ppm/°C.

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