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A new low-loss dielectric using $CaTiO_3$-modified $(Mg_{0.95}Mn_{0.05})TiO_3$ ceramics for microwave applications

Cheng-Liang Huang*, Jhih-Yong Chen, Guan-Sian Huang

Department of Electrical Engineering, National Cheng Kung University, No. 1 University Road, Tainan 70101, Taiwan

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ABSTRACT

The microwave dielectric properties of the $(1-x)(Mg_{0.95}Mn_{0.05})TiO_3$–$xCaTiO_3$ ceramic system prepared by mixed oxide route have been investigated. The microstructures of the ceramics were characterized by SEM. Ilmenite-structured $(Mg_{0.95}Mn_{0.05})TiO_3$ and perovskite-structured $CaTiO_3$ were coexisted and the two-phase system was confirmed by the XRD and EDX analysis. The microwave dielectric properties are strongly related to the density and matrix of the specimen. Combination of $(Mg_{0.95}Mn_{0.05})TiO_3$ and $CaTiO_3$ 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, $0.93(Mg_{0.95}Mn_{0.05})TiO_3$–$0.07CaTiO_3$ possesses excellent microwave dielectric properties with a dielectric constant (ε_r) of ~22.67, a $Q \times f$ of ~90,700 GHz (where f = 9 GHz, is the resonant frequency) and a τ_f value of ~0.8 ppm/°C at 1270 °C for 4 h. It is proposed as a suitable material candidate for applications requiring low microwave 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 [3,4]. 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 used of dielectric resonator and microwave device substrate [5–7]. For instance, low-loss dielectrics with different dielectric constants have become the most popular materials used for today's GPS patch antennas [8].

$MgTiO_3$-based ceramics has wide applications as dielectrics in resonators, filters and antennas for communication, radar and global positioning systems (GPS) operating at microwave frequencies. $MgTiO_3$–$CaTiO_3$ ceramics is well known as the material for temperature compensating type capacitor, dielectric resonator and patch antenna. With the ratio Mg:Ca = 95:5, $0.95MgTiO_3$–$0.05CaTiO_3$ ceramics gives ε_r ~21, $Q \times f$ value ~56,000 GHz measured at 7 GHz and a zero τ_f value [9]. $MgTiO_3$ and $MnTiO_3$ formed the solid solutions of the magnesium manganese titanates easily because of their same ilmenite-structure and similar ionic radius (Mg^{2+} = 0.72 Å, Mn^{2+} = 0.83 Å) [10]. The $(Mg_{0.95}Mn_{0.05})TiO_3$ ($\varepsilon_r \sim 17$, $Q \times f \sim 220{,}000$ GHz, $\tau_f \sim -58$ ppm/°C) [11] dielectric was reported to possess an excellent $Q \times f$. However, it also suffers from a large negative τ_f, which limits its practical applications. To combine it with a compound having a positive τ_f should be the most convenient and promising way to achieve a zero τ_f [12].

In this paper, $CaTiO_3$ ($\varepsilon_r \sim 170$, $Q \times f \sim 3600$ GHz and $\tau_f \sim 800$ ppm/°C) [13] was employed as a τ_f compensator, and was added to $(Mg_{0.95}Mn_{0.05})TiO_3$ to form a new ceramic system $(1-x)(Mg_{0.95}Mn_{0.05})TiO_3$–$xCaTiO_3$ to further improve the microwave dielectric properties of the specimens in particular, the τ_f value. The dielectric properties at microwave frequencies of the sintered ceramics were characterized and discussed in terms of the densification 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.

2. Experimental procedure

Sample of $(Mg_{0.95}Mn_{0.05})TiO_3$ and $CaTiO_3$ were separately synthesized by conventional solid state method from individual high-purity oxide powders (>99.9%): MgO, MnO, $CaCO_3$ and TiO_2. The starting materials were mixed according to the desired stoichiometry $(Mg_{0.95}Mn_{0.05})TiO_3$ and $CaTiO_3$. The powders were ground in distilled water for 24 h in a ball mill with agate balls. All mixtures were dried and passed through a 100-mesh sieve. The $(Mg_{0.95}Mn_{0.05})TiO_3$ and $CaTiO_3$ powders were calcined at 1100 °C for 4 h in air. After calcinations, the calcined $(Mg_{0.95}Mn_{0.05})TiO_3$ and $CaTiO_3$ powders were mixed according to the molar fraction $(1-x)(Mg_{0.95}Mn_{0.05})TiO_3$–$xCaTiO_3$ (x = 0.05–0.1) and then re-milled for 24 h.

* Corresponding author. Tel.: +886 6 2757575x62390; fax: +886 6 2345482.
E-mail address: huangcl@mail.ncku.edu.tw (C.-L. Huang).

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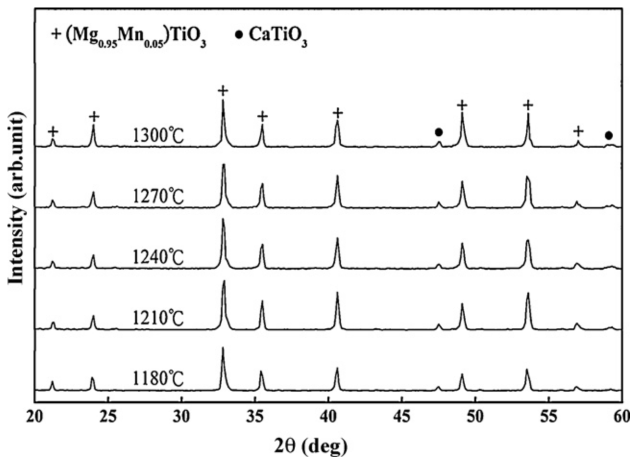

Fig. 1. X-ray diffraction patterns of $0.93(Mg_{0.95}Mn_{0.05})TiO_3$–$0.07CaTiO_3$ ceramics sintered at different temperatures for 4 h.

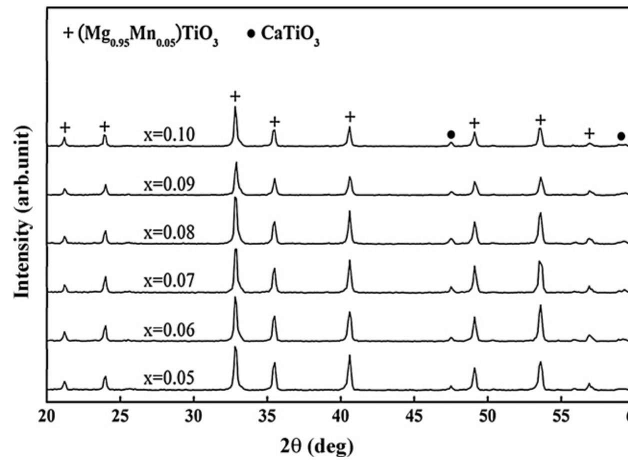

Fig. 2. X-ray diffraction patterns of $(1-x)(Mg_{0.95}Mn_{0.05})TiO_3$–$xCaTiO_3$ ceramic system sintered at 1270 °C for 4 h with different x values.

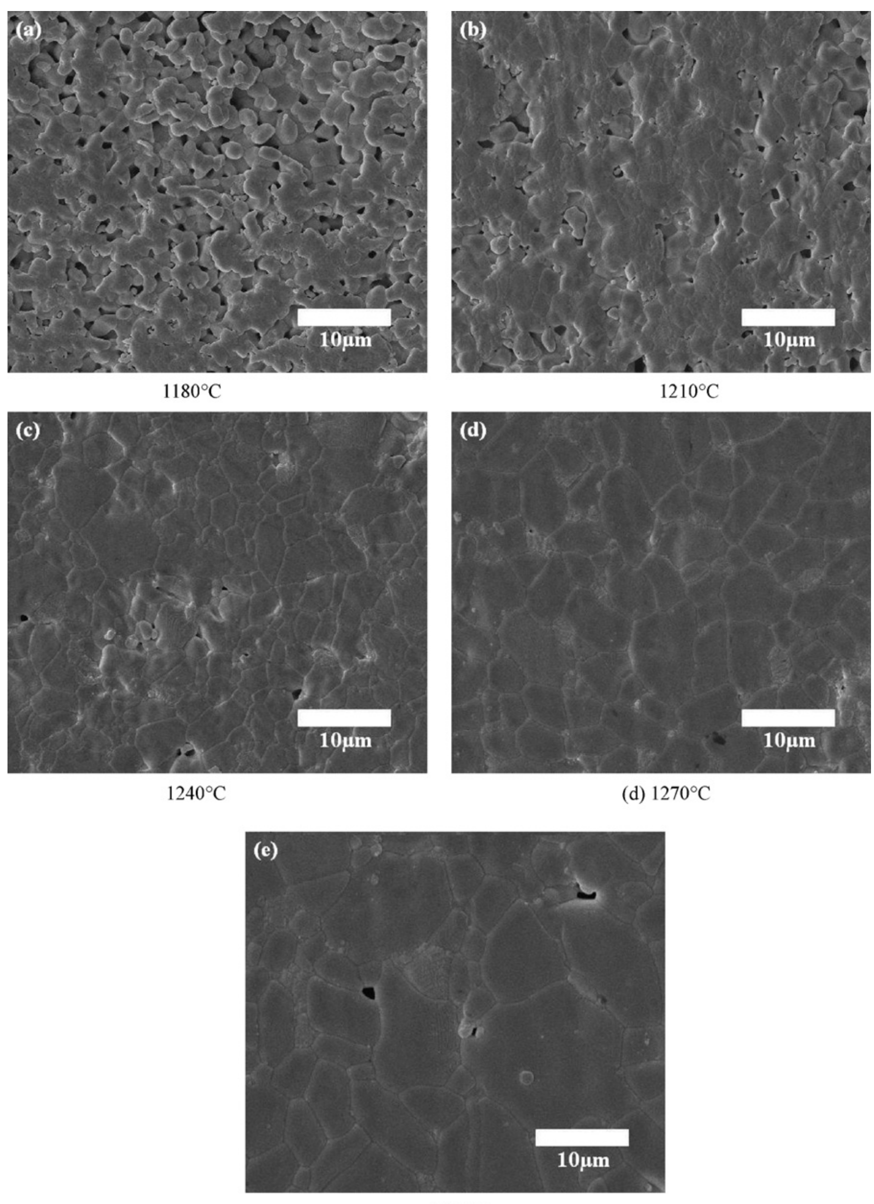

Fig. 3. SEM micrographs of $0.93(Mg_{0.95}Mn_{0.05})TiO_3$–$0.07CaTiO_3$ ceramics sintered at (a) 1180 °C, (b) 1210 °C, (c) 1240 °C, (d) 1270 °C and (e) 1300 °C for 4 h.

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 1180–1300 °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 microstructures were evaluated for thermal-etched surfaces by scanning electron microscopy (SEM; Philips XL-40FEG) and an energy-dispersive X-ray spectrometer (EDS). The apparent densities of the sintered specimens, as a function of sintering temperature were 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 [14,15]. A system combining a HP8757D network analyzer (Palo Alto, CA) and a HP8350B sweep oscillator (Palo Alto, CA) was employed in the measurement. An identical technique was applied to the measurement of the temperature coefficient of resonant frequency (τ_f). The test set was placed over a thermostat in the temperature range of 25–80 °C. τ_f (ppm/°C) can be calculated by considering the change in resonant frequency (Δf).

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

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 0.93($Mg_{0.95}Mn_{0.05}$)TiO_3–0.07$CaTiO_3$ (hereafter referred to as 93MMCT) ceramics sintered at different temperatures for 4 h. The XRD patterns showed that peaks indicating the presence of ($Mg_{0.95}Mn_{0.05}$)TiO_3 as the main crystalline phase, in association with $CaTiO_3$ as a minor phase. It is understood that crystal structures of ($Mg_{0.95}Mn_{0.05}$)TiO_3 and $CaTiO_3$ are rhombohedral (ICDD-PDF #00-006-0494) and cubic

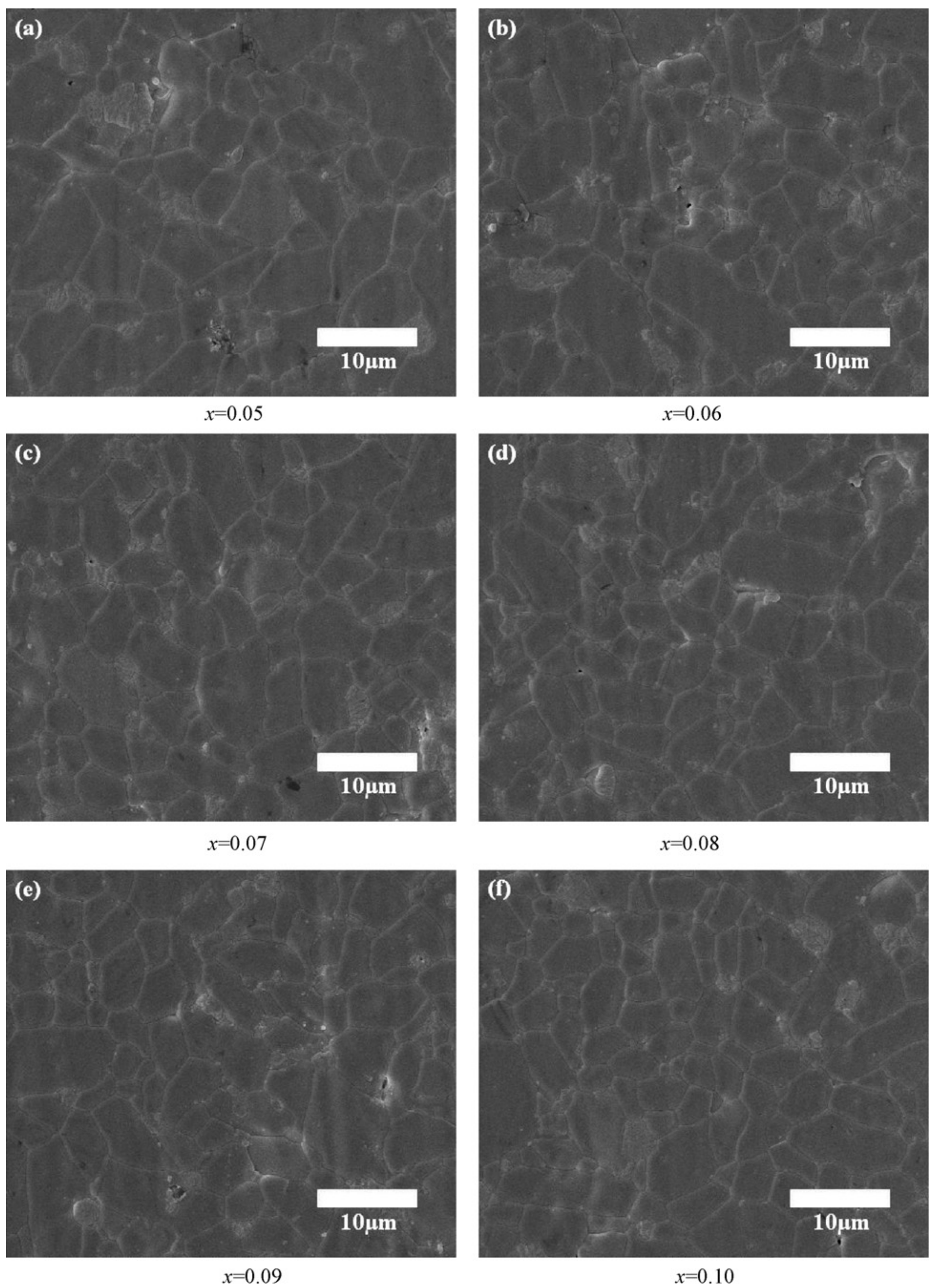

Fig. 4. SEM micrographs of the $(1-x)(Mg_{0.95}Mn_{0.05})TiO_3$–$xCaTiO_3$ ceramic system with x= (a) 0.05, (b) 0.06, (c) 0.07, (d) 0.08, (e) 0.09 and (f) 0.1 sintered at 1270 °C for 4 h.

perovskite [8], respectively. The XRD patterns of the 93MMCT ceramic system did not change markedly with sintering temperatures in the range of 1180–1300 °C. Moreover, XRD patterns of the $(1-x)(Mg_{0.95}Mn_{0.05})TiO_3$–$xCaTiO_3$ ceramic system are shown in Fig. 2 suggesting the intensity of the $(Mg_{0.95}Mn_{0.05})TiO_3$ phase was lowered as the x increased.

The SEM micrographs of thermal-etched 93MMCT ceramics sintered at different temperatures for 4 h are illustrated in Fig. 3. As the sintering temperature increased, the grain size increased. The pores were almost eliminated for specimen sintered at 1240 °C and a well-developed microstructure could be achieved at 1270 °C. However, rapid grain growth resulting in an inhomogeneous morphology was observed at 1300 °C leading to a presence of pores. It might also lead to a degradation in the microwave dielectric properties of the ceramics. In addition, SEM micrographs of the $(1-x)(Mg_{0.95}Mn_{0.05})TiO_3$–$xCaTiO_3$ system with different x values sintered at 1270 °C are illustrated in Fig. 4. The average grain size of the ceramics decreased with the increase of the $CaTiO_3$ content. From the EDX analysis, the EDX datum of spots A and B were showed in Fig. 5(b). Energy-dispersive X-ray (EDX) analysis was used in combination with scanning electron microscopy to try to distinguish each grain for 93MMCT ceramics sintered at 1270 °C, as shown in Fig. 5(a). The grain morphology of 93MMCT ceramics exhibited two types of grains: large grains (spot A) were $(Mg_{0.95}Mn_{0.05})TiO_3$ and small cubic-shape grains (spot B) were $CaTiO_3$. Not only did it confirm the formation of a two-phase system, but it also explained the reduce of the average grain size of the ceramics as the $CaTiO_3$ phase increased was due to the fact that $CaTiO_3$ shows a relatively small grain size.

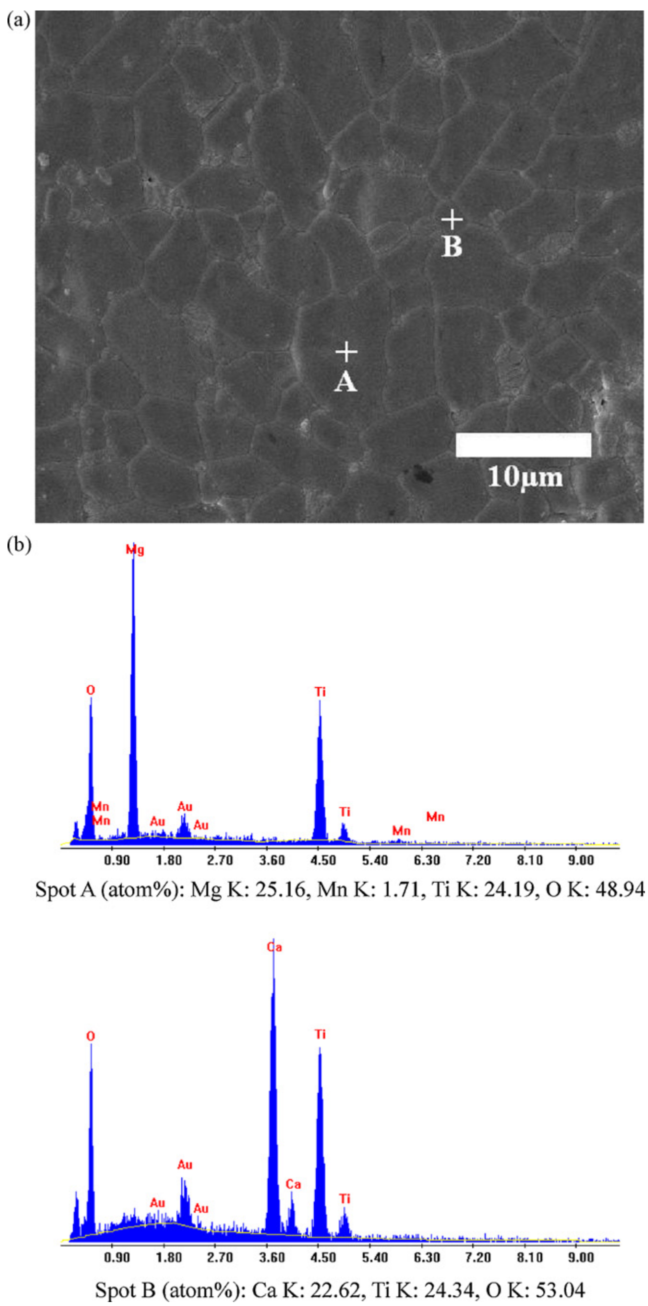

Fig. 5. (a) The marks of SEM for the $0.93(Mg_{0.95}Mn_{0.05})TiO_3$–$0.07CaTiO_3$ ceramics sintered at 1270 °C. (b) EDX datum of $0.93(Mg_{0.95}Mn_{0.05})TiO_3$–$0.07CaTiO_3$ ceramics for spots A and B.

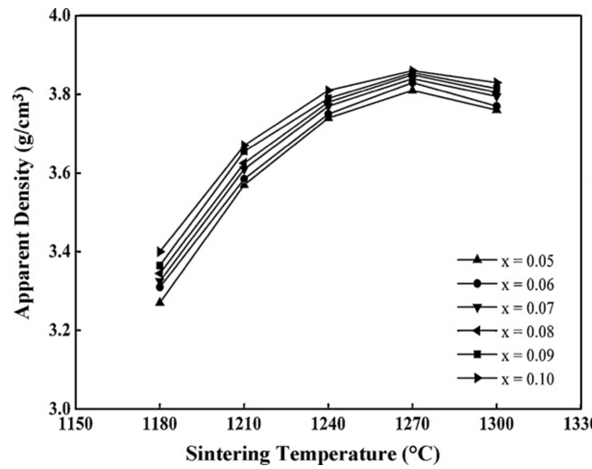

Fig. 6. Apparent density of $(1-x)(Mg_{0.95}Mn_{0.05})TiO_3$–$xCaTiO_3$ ceramic system as a function of its sintering temperature.

The apparent densities of $(1-x)(Mg_{0.95}Mn_{0.05})TiO_3$–$xCaTiO_3$ ceramic system sintered at different temperatures for 4 h are shown in Fig. 6. The density for the specimen sintered at 1180 °C was low, but increased with increasing sintering temperature to a maximum and then slightly declined thereafter, which may have been caused by the presence of the pores induced by the over-sintering. For specimen using 93MMCT, a maximum density of 3.84 g/cm^3 can be achieved at 1270 °C.

Fig. 7 shows the dielectric constants of $(1-x)(Mg_{0.95}Mn_{0.05})TiO_3$–$xCaTiO_3$ ceramic system sintered at different temperatures

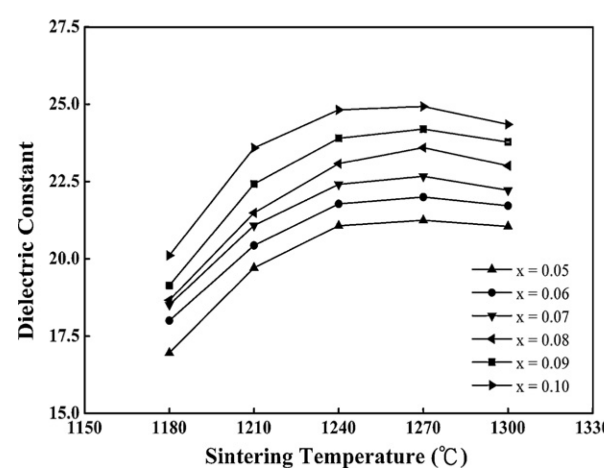

Fig. 7. Dielectric constant of $(1-x)(Mg_{0.95}Mn_{0.05})TiO_3$–$xCaTiO_3$ ceramic system as a function of its sintering temperature.

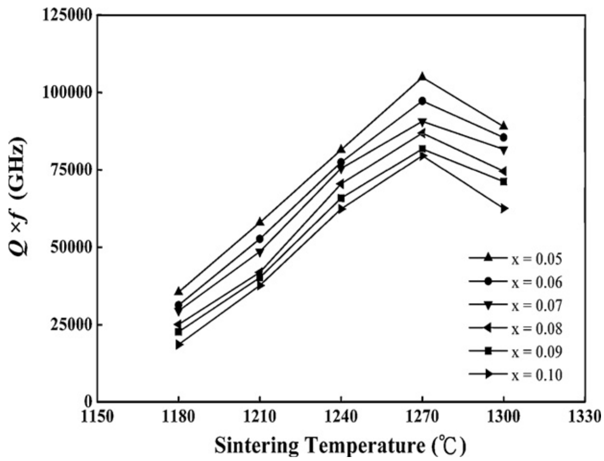

Fig. 8. $Q \times f$ value of $(1-x)(Mg_{0.95}Mn_{0.05})TiO_3$–$xCaTiO_3$ ceramic system as a function of its sintering temperature.

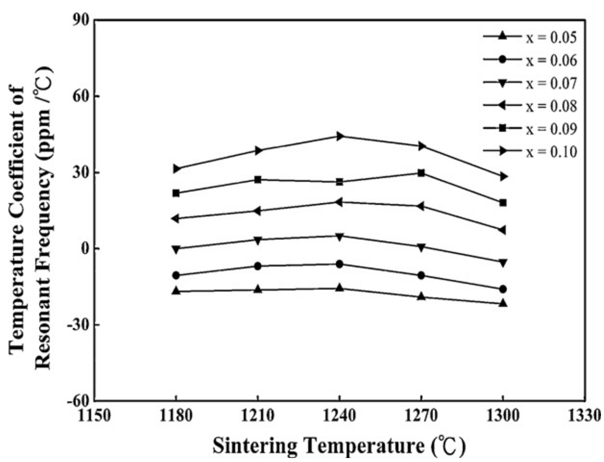

Fig. 9. τ_f value of $(1-x)(Mg_{0.95}Mn_{0.05})TiO_3$–$xCaTiO_3$ ceramic system as a function of its sintering temperature.

for 4 h. Variation of ε_r value was consistent with that of density. The dielectric constant of 93MMCT increased with increasing sintering temperature. After reaching its maximum at 1270 °C, it decreased. A maximum ε_r value of 22.67 was obtained for 93MMCT ceramics sintered at 1270 °C for 4 h. It indicated higher sintering temperature does not necessarily lead the specimen to a higher dielectric constant. In addition, the increase in the dielectric constant at higher x values was due to the presence of more $CaTiO_3$ phase which has a relatively high dielectric constant.

The $Q \times f$ of $(1-x)(Mg_{0.95}Mn_{0.05})TiO_3$–$xCaTiO_3$ ceramic system sintered at different temperatures for 4 h is demonstrated in Fig. 8. By increasing the sintering temperature, the $Q \times f$ value of 93MMCT 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 $Q \times f$ value of 90,700 GHz (at 9 GHz), showing a 62% increase compared with that of $0.95MgTiO_3$–$0.05CaTiO_3$ ceramics, is obtained for the 93MMCT ceramics sintered at 1270 °C for 4 h. It also indicated a 130 °C lowering in its sintering temperature. The degradation of $Q \times f$ value was attributed to the over-sintering resulted in a reduction of density as observed in Figs. 3 and 6. The microwave dielectric loss is caused not only by the lattice vibrational modes, but also by the pores, the second phases, the impurities, the lattice defect, or the density [16–18]. The dielectric loss of the 93MMCT ceramics, in our case, is mainly dominated by the density.

Fig. 9 illustrates the temperature coefficients of resonant frequency (τ_f) of $(1-x)(Mg_{0.95}Mn_{0.05})TiO_3$–$xCaTiO_3$ ceramic system sintered at 1180–1300 °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. By increasing $CaTiO_3$, the τ_f value varied toward positive direction. This is because adding $CaTiO_3$ renders a large positive τ_f value (800 ppm/°C). Through appropriate adjustment, a near-zero τ_f (~0.8 ppm/°C) can be obtained for 93MMCT specimen at 1270 °C for 4 h.

4. Conclusion

$(1-x)(Mg_{0.95}Mn_{0.05})TiO_3$–$xCaTiO_3$ ceramic system showed mixed phases of $(Mg_{0.95}Mn_{0.05})TiO_3$ as the main phase in association with the minor phase $CaTiO_3$. The microwave dielectric properties are strongly related to the density and the matrix of the specimen. With $x = 0.07$, near-zero τ_f value can be obtained for $(1-x)(Mg_{0.95}Mn_{0.05})TiO_3$–$xCaTiO_3$ ceramic system. An excellent combination of microwave dielectric properties with a dielectric constant ε_r of ~22.67, a $Q \times f$ value of ~90,700 GHz (measured at 9 GHz) and a τ_f value of ~0.8 ppm/°C was obtained for 93MMCT ceramics sintered at 1270 °C for 4 h. Therefore, 93MMCT is suitable for applications in microwave dielectric resonators and filters because of its excellent microwave dielectric properties.

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