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Phase, microstructure, and microwave dielectric properties of a new ceramic system: $(1-x)Mg(Ti_{0.95}Sn_{0.05})O_3$–$xCaTiO_3$

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ABSTRACT

The microwave dielectric properties and microstructure of the new ceramic system $(1-x)Mg(Ti_{0.95}Sn_{0.05})O_3$–$xCaTiO_3$ ($0.02 \le x \le 0.08$) prepared via a mixed-oxide route were investigated. To attain a temperature-stable material, $CaTiO_3$ was added to $Mg(Ti_{0.95}Sn_{0.05})O_3$ as a temperature coefficient of resonant frequency (τ_f) compensator. The compositions with $0.02 \le x \le 0.08$ resulted in a mixture of two phases, $Mg(Ti_{0.95}Sn_{0.05})O_3$ and $CaTiO_3$, as confirmed by X-ray diffraction and energy-dispersive X-ray spectroscopic analyses. The values of the dielectric constant (ε_r) and the τ_f of the ceramics were found to increase, and the unloaded quality factor ($Q_u f_o$) was found to decrease with increasing x values (i.e., increasing $CaTiO_3$ content). Excellent microwave dielectric properties of $\varepsilon_r \approx 21.5$, $Q_u f_o \approx 112{,}500$ GHz (at 9 GHz), and $\tau_f \approx 1.1$ ppm/°C were attained for the $0.94\{Mg(Ti_{0.95}Sn_{0.05})O_3\}$–$0.06CaTiO_3$ ceramic sintered at 1375 °C for 4 h.

1. Introduction

Over the past four decades, numerous microwave dielectric ceramics have been investigated to evaluate their suitability for use in the growing array of wireless communication systems. To be suitable for use in practical applications, microwave dielectric materials must exhibit three key characteristics: a high dielectric constant (ε_r), a high unloaded quality factor (generally termed as $Q_u f_o$) for selectivity, and a near-zero temperature coefficient of resonant frequency (τ_f) for stability [1]. Various dielectric materials that exhibit the aforementioned attributes have been studied. However, in such cases, the working frequency bands have been changed to higher frequencies, such as from 900 MHz to 2.4, 5.2, or even 5.8 GHz, which limits the use of high-ε_r materials [2]. For high-frequency materials, a near-zero τ_f remains one of the essential requirements and becomes more critical as the operating frequency increases.

Two conventional approaches are generally employed for developing ceramic with excellent dielectric properties: mixing two or more materials to achieve property compensation and creating new materials. Mixing of two or more materials with different dielectric properties is more popular because of its simplicity. That is, to achieve a material with $\tau_f \approx 0$, the mixing of two different materials with positive and negative τ_f values to form mixed phases or a solid solution is the easier and more promising approach [3–8].

Magnesium titanate ($MgTiO_3$) with an ilmenite-type structure with trigonal $R3$ space symmetry is a leading dielectric material that has attracted much attention because of its low cost and good combination of dielectric properties. Because of their low dielectric loss, $MgTiO_3$-based ceramics have been widely applied as dielectrics in resonators, filters, and antennas for communications, radar, and global positioning systems operating at microwave frequencies. The $Mg(Ti_{0.95}Sn_{0.05})O_3$ ceramic, in which Ti^{4+} has been partially replaced with Sn^{4+}, has been reported to exhibit an excellent combination of dielectric properties ($\varepsilon_r \approx 17.7$ and $Q_u f_o \approx 276{,}000$ GHz) [9]. Although the $Mg(Ti_{0.95}Sn_{0.05})O_3$ ceramic exhibits an excellent $Q_u f_o$ value, it also exhibits a large, negative τ_f value ($\tau_f \approx -43$ ppm/°C), which limits its practical applications. To achieve a near-zero τ_f for the $Mg(Ti_{0.95}Sn_{0.05})O_3$ ceramic, combining it with a material with a positive τ_f value is the most convenient and promising approach.

The aim of the present study was to tune the τ_f value of the $Mg(Ti_{0.95}Sn_{0.05})O_3$ ceramic to approach zero. $CaTiO_3$ ($\varepsilon_r \approx 170$, $Q_u f_o \approx 3600$ GHz, and $\tau_f \approx 800$ ppm/°C) [10] was used as a τ_f compensator because of its high positive τ_f value and was added to the $Mg(Ti_{0.95}Sn_{0.05})O_3$ ceramic to form a new ceramic system: $(1-x)Mg(Ti_{0.95}Sn_{0.05})O_3$–$xCaTiO_3$ (MSTCT). The phase, microstructure, and microwave dielectric properties of the MSTCT ceramic system are discussed extensively.

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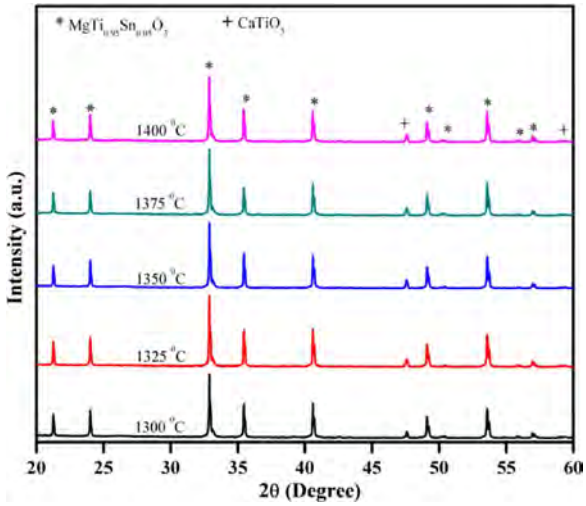


Fig. 1. Powder XRD patterns of $0.94\{Mg(Ti_{0.95}Sn_{0.05})O_3\}–0.06CaTiO_3$ ceramic samples sintered at different temperatures for 4 h.

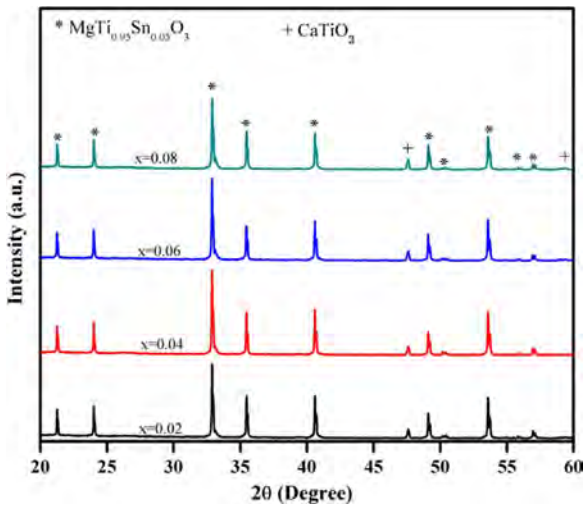


Fig. 2. Powder XRD patterns of $(1 - x)Mg(Ti_{0.95}Sn_{0.05})O_3–xCaTiO_3$ $(0.02 \le x \le 0.08)$ ceramics sintered at 1375 °C for 4 h.

2. Experimental procedure

The samples of $Mg(Ti_{0.95}Sn_{0.05})O_3$ and $CaTiO_3$ were synthesized individually via a conventional solid-state method using high-purity oxide powders (> 99.90%) of MgO, TiO_2, SnO_2, and $CaCO_3$. The powders were weighed in the desired stoichiometric ratio, combined, and then milled in ethanol for 24 h with zirconia balls as the grinding medium using a ball-milling machine. The resultant slurries were dried in oven at 100 °C and then passed through a 200-mesh sieve to obtain fine powders. The fine powders were calcined at 1200 °C for 5 h at heating/cooling rates of 5 °C/min. After calcination, the $Mg(Ti_{0.95}Sn_{0.05})O_3$ and $CaTiO_3$ powders were mixed to the desired composition $(1 - x)Mg(Ti_{0.95}Sn_{0.05})O_3–xCaTiO_3$ $(0.02\ x \le 0.08)$ and then re-milled for 24 h followed by the addition of 5 wt% of PVA as binder. The fine calcined powders were pressed isostatically at 150 MPa. The green-body pellets were initially heated at 600 °C for 2 h to remove the binder and were then sintered at 1300–1400 °C for 4 h in air.

The bulk densities of the sintered pellets were measured using the Archimedes method. X-ray diffraction (XRD, PANalytical Expert PRO) was used to examine the crystalline phases of the sintered samples. For microstructural observations, the sintered samples were polished and thermally etched for 30 min at temperatures 10% lower than their corresponding sintering temperatures. Field-emission scanning electron microscopy (FESEM, JSEM-5610LV, Japan) and energy-dispersive X-ray spectrometry (EDS) were used to observe the microstructure and to analyze the elemental composition, respectively, of the sintered materials.

The $Q_u f_o$ values and the ε_r were measured via the Hakki–Coleman dielectric resonator method using an Agilent 8722ET (50 MHz to 40 GHz) network analyzer. The τ_f values were calculated using Eq. (1) by noting the variations in the resonant frequencies of the TE_{011} resonant mode over the temperature range from 25 °C to 85 °C:

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

where f_1 and f_2 are the resonant frequencies at temperatures T_1 (25 °C) and T_2 (85 °C), respectively.

3. Results and discussion

Powder XRD patterns of $0.94\{Mg(Ti_{0.95}Sn_{0.05})O_3\}–0.06CaTiO_3$ (hereafter referred to as 6MSTCT) ceramic samples sintered for 4 h at temperatures ranging from 1300 °C to 1400 °C are illustrated in Fig. 1. The diffraction peaks revealed the presence of $Mg(Ti_{0.95}Sn_{0.05})O_3$ as the major crystalline phase, accompanied by a minor $CaTiO_3$ phase. The formation of a mixture of two phases was because of their different structures and because of the large difference in ionic radius between Ca^{2+} (1.00 Å) and Mg^{2+} (0.72 Å) [11]. No remarkable difference was observed among the XRD patterns of the 6MSTCT ceramics sintered at different temperatures. The powder XRD patterns of the MSTCT ceramic system sintered at 1375 °C for 4 h are shown in Fig. 2.

The microstructures of the 6MSTCT ceramics sintered at different temperatures for 4 h are shown in Fig. 3. A porous microstructure was observed for the sample sintered at 1300 °C; however, as the sintering temperature was increased beyond 1300 °C, pores were eliminated, and the grain size increased. A well-developed microstructure was observed at 1375 °C. However, a further increase of the sintering temperature resulted in rapid grain growth, leading to pore formation, which might degrade the microwave dielectric performance of the ceramics. The microstructures of the MSTCT ceramics with different x values and sintered at 1375 °C for 4 h are shown in Fig. 4. Because of the narrow compositional range $(0.02 \le x \le 0.08)$, no specific change was observed in the grain size.

Fig. 5 shows the EDS results of 6MSTCT ceramics sintered at 1400 °C for 4 h. The grain morphology of the 6MSTCT ceramics indicated two different grain types. The small cubic-shaped grains labeled as A are rich in Ca and Ti but poor in Mg, whereas large round grains labeled as B are rich in Mg and Ti but poor in Ca. On the basis of the EDS results, the small cube-shaped grains are clearly $CaTiO_3$, whereas the large round grains are $Mg(Ti_{0.95}Sn_{0.05})O_3$. These results are in good agreement with the results of the XRD analyses.

Fig. 6 shows the variation in the apparent densities of the MSTCT ceramics as a function of the sintering temperature. The density of the sintered samples of the MSTCT ceramics increased with increasing sintering temperature, eventually reaching a maximum at 1375 °C. The increase in density with increasing sintering temperature was due to the decrease in the porosity and increase in grain growth, which resulted in a dense microstructure, as shown in Fig. 4. However, a slight decrease in density was observed when the sintering temperature was increased to 1400 °C, possibly because of the formation of a porous microstructure due to rapid grain growth. The variation in the density of the MSTCT ceramics is explained on the basis of the changes in the microstructure with increasing sintering temperature. The maximum density attained for the 6MSTCT ceramics was 3.80 g/cm^3 at 1375 °C; this density is about 95% of the theoretical density calculated on the basis of the XRD analysis.

The variation in the dielectric constants of the MSTCT ceramics as a function of sintering temperature is shown in Fig. 7. The variation of ε_r

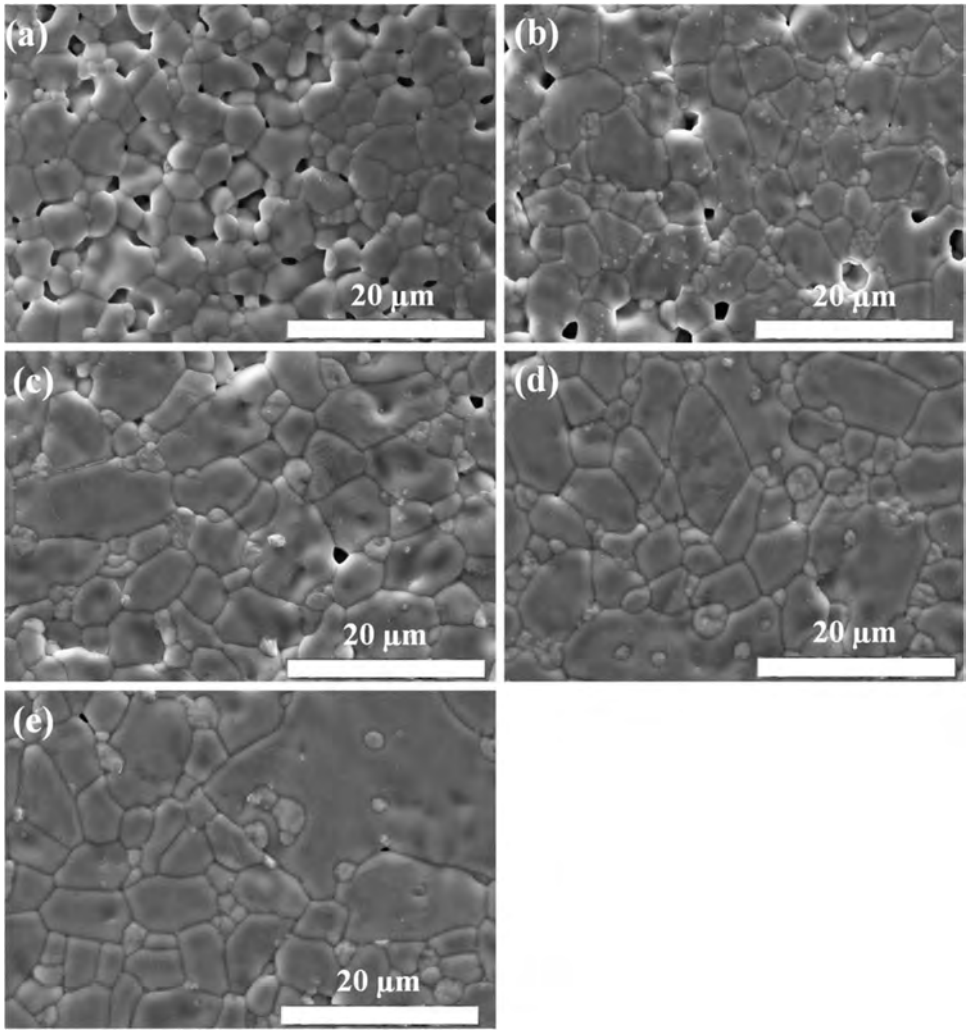


Fig. 3. SEM micrographs of $0.94\{Mg(Ti_{0.95}Sn_{0.05})O_3\}–0.06CaTiO_3$ ceramics sintered for 4 h at various temperatures: (a) 1300 °C, (b) 1325 °C, (c) 1350 °C, (d) 1375 °C, and (e) 1400 °C.

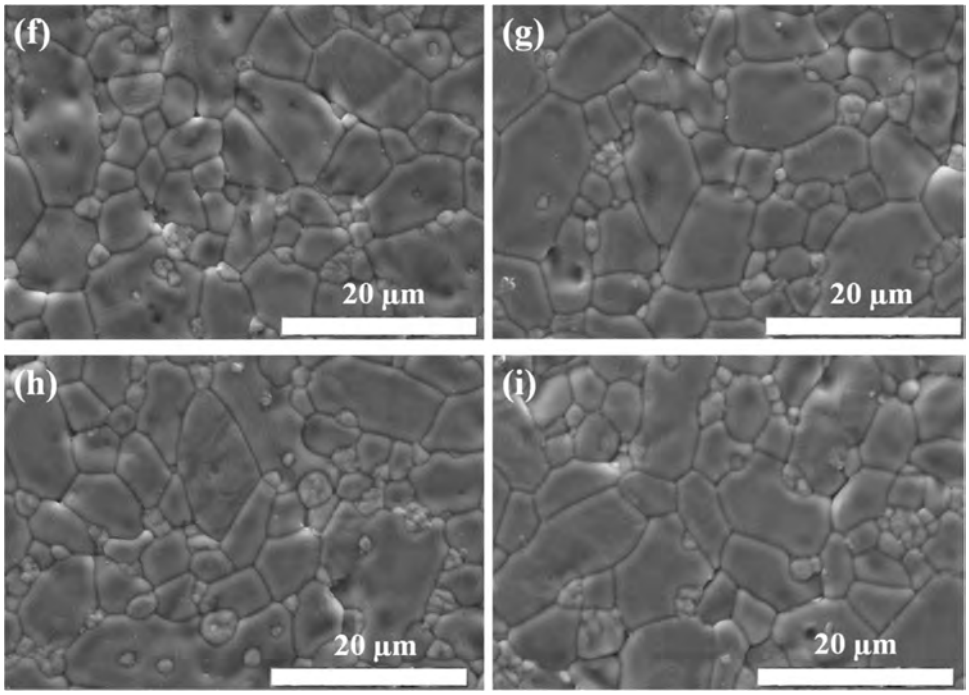
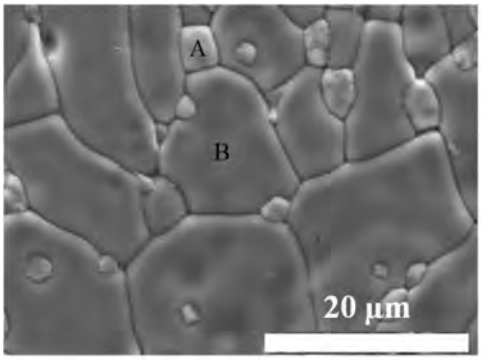


Fig. 4. SEM micrographs of $(1 – x)Mg(Ti_{0.95}Sn_{0.05})O_3–xCaTiO_3$ ceramics sintered at 1375 °C for 4 h: (f) $x = 0.02$, (g) $x = 0.04$, (h) $x = 0.06$, and (i) $x = 0.08$.



	Atom (%)				
Grain	Mg K	Sn K	Ca K	Ti K	O K
A	0	0	22.75	21.27	55.98
B	22.68	0.78	0	21.69	54.85

Fig. 5. EDS results for the 0.94{$Mg(Ti_{0.95}Sn_{0.05})O_3$}–0.06$CaTiO_3$ ceramic sintered at 1400 °C for 4 h.

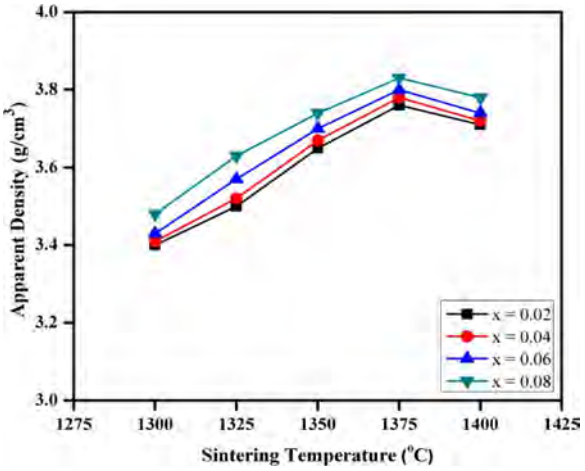


Fig. 6. Variation in the apparent density of $(1-x)Mg(Ti_{0.95}Sn_{0.05})O_3$–$xCaTiO_3$ ($0.02 \le x \le 0.08$) ceramics as a function of the sintering temperature.

with sintering temperature was consistent with the variation of the density. With increasing sintering temperature, the ε_r first increased, reached a maximum at 1375 °C, and then decreased. Moreover, the ε_r increased with increasing $CaTiO_3$ content because $CaTiO_3$ has an ε_r substantially greater than that of $Mg(Ti_{0.95}Sn_{0.05})O_3$. The ε_r value of the MSTCT ceramics increased from 19.1 to 22.7 as x was increased from 0.02 to 0.08, which demonstrates that the ε_r of the MSTCT ceramics varied not only with the sintering temperature but also with the $CaTiO_3$ content.

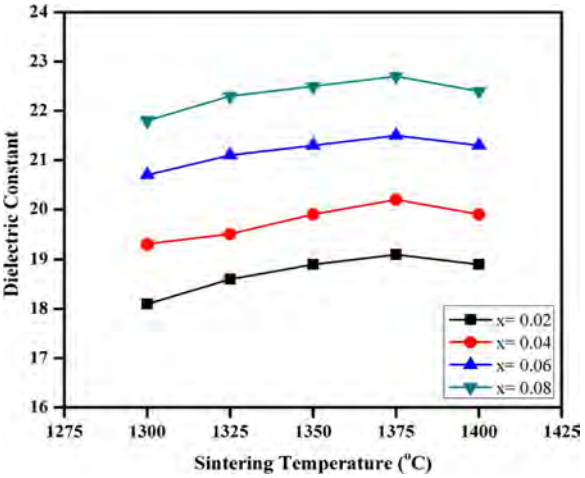


Fig. 7. Variation in the dielectric constant of the $(1-x)Mg(Ti_{0.95}Sn_{0.05})O_3$–$xCaTiO_3$ ($0.02 \le x \le 0.08$) ceramics as a function of sintering temperature.

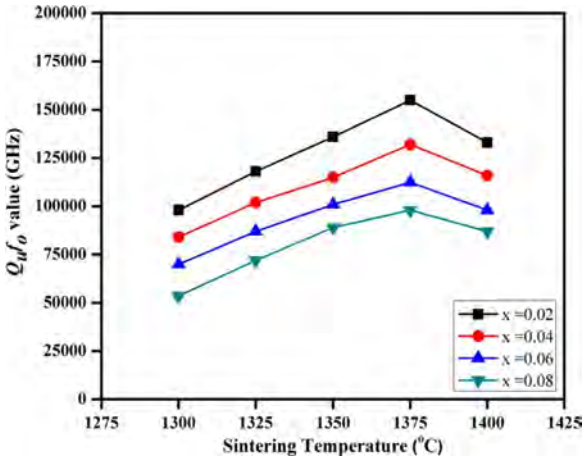


Fig. 8. Variation in the $Q_u f_o$ value of $(1-x)Mg(Ti_{0.95}Sn_{0.05})O_3$–$xCaTiO_3$ ($0.02 \le x \le 0.08$) ceramics as a function of the sintering temperature.

The variation of the $Q_u f_o$ value of the MSTCT ceramics with the sintering temperature is shown in Fig. 8. The $Q_u f_o$ value of the MSTCT ceramics increased with increasing sintering temperature, reached a maximum value at 1375 °C, and decreased as the sintering temperature was increased further. The maximum $Q_u f_o$ value attained for the 6MSTCT ceramic was 112,500 GHz (at 9 GHz) for the sample sintered at 1375 °C for 4 h. The decrease of the $Q_u f_o$ value at higher sintering temperatures is attributed to inhomogeneous grain growth due to over-sintering, which resulted in a decrease in density. The trend of the $Q_u f_o$ values of the MSTCT ceramics is the same as that of the density values because densification of ceramic materials strongly affects their dielectric loss. The lattice vibrational modes are not the only factor that affects the microwave dielectric loss; the second phase, pores, impurities, and density can also affect the dielectric loss [12–15]. The $Q_u f_o$ value of the MSTCT ceramics decreases as the $CaTiO_3$ content increases from 0.02 to 0.08. This decrease of the $Q_u f_o$ value with increasing $CaTiO_3$ content is attributable to the large difference in the $Q_u f_o$ values of $Mg(Ti_{0.95}Sn_{0.05})O_3$ and $CaTiO_3$; the same phenomenon has been observed for other microwave dielectric materials [5,6].

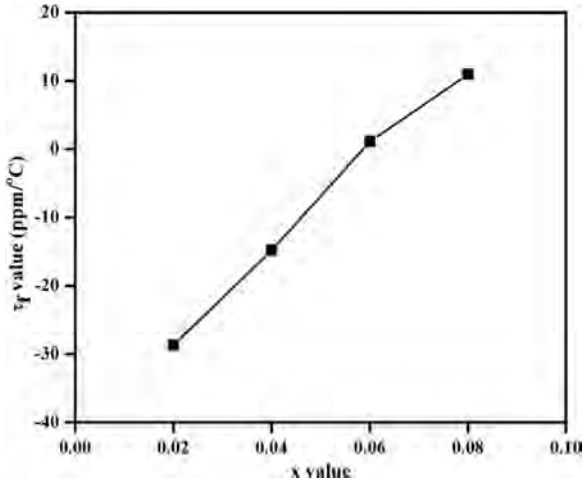


Fig. 9. Variation of the τ_f value of $(1-x)Mg(Ti_{0.95}Sn_{0.05})O_3$–$xCaTiO_3$ ceramics sintered at 1375 °C for 4 h as a function of x.

Fig. 9 shows the τ_f value as a function of x of the MSTCT ceramics sintered at 1375 °C for 4 h. The τ_f values of mixed materials are well known to be correlated to the second phase, additives, and the compositions of the materials [6]. Because $CaTiO_3$ possesses a large τ_f value ($\tau_f \approx 800$ ppm/°C), the τ_f value of MSTCT ceramics rapidly increased with increasing $CaTiO_3$ content. As the $CaTiO_3$ content was increased from 0.02 to 0.08, the τ_f value of MSTCT ceramics shifted toward more positive values, which shows that a near-zero τ_f can be attained by adjusting the $CaTiO_3$ content.

4. Conclusion

The MSTCT ceramic system was composed of two phases of $Mg(Ti_{0.95}Sn_{0.05})O_3$ as the major phase in association with a minor phase of $CaTiO_3$. With increasing $CaTiO_3$ content, the ε_r and τ_f values of the MSTCT ceramics were enhanced, whereas the $Q_u f_o$ value decreased. As the $CaTiO_3$ content (x value) was increased from 0.02 to 0.08, the dielectric constant increased from 19.1 to 22.7, the $Q_u f_o$ value decreased from 155,000 GHz (at 9 GHz) to 98,000 GHz (at 9 GHz), and the τ_f value increased from −28.7 ppm/°C to +11 ppm/°C. Excellent microwave dielectric properties $\varepsilon_r \approx 21.5$, $Q_u f_o \approx 112{,}500$ GHz (at 9 GHz), and $\tau_f \approx 1.1$ ppm/°C were attained for the 6MSTCT ceramic sintered at 1375 °C for 4 h.

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