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Microstructure and microwave dielectric properties of $(1-x)Ca_{0.6}La_{0.267}TiO_3$–$xCa(Mg_{1/3}Nb_{2/3})O_3$ ceramics

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Abstract

$(1-x)Ca_{0.6}La_{0.267}TiO_3$–$xCa(Mg_{1/3}Nb_{2/3})O_3$ ceramics were prepared by a conventional solid-state ceramic route. The microstructure and microwave dielectric properties were investigated as a function of composition and sintering temperature. As the content of $Ca(Mg_{1/3}Nb_{2/3})O_3$ increased, the temperature coefficient of resonant frequency (τ_f) value decreased gradually. By appropriately adjusting the x value in the present ceramic system, a near-zero τ_f value could be achieved. The appropriate increase of sintering temperature could significantly improve $Q{\cdot}f$ value by influencing the grain growth. The optimal microwave dielectric properties with a dielectric constant (ε_r) of 52.4, $Q{\cdot}f$ of 36,428 GHz (at 5.8 GHz), and τ_f of 3.4 ppm/°C were obtained for the specimen $0.5Ca_{0.6}La_{0.267}TiO_3$–$0.5Ca(Mg_{1/3}Nb_{2/3})O_3$ sintered at 1490 °C for 4 h.
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Keywords: C. Dielectric properties; $(1-x)Ca_{0.6}La_{0.267}TiO_3$–$xCa(Mg_{1/3}Nb_{2/3})O_3$; Complex perovskite; Ceramics

1. Introduction

The applications of the microwave dielectric ceramics have been rapidly increasing in the field of mobile communication such as resonators, filters and antennas [1,2]. The principal important properties required for microwave dielectric ceramics are as follows: a high dielectric constant (ε_r) to reduce the size of devices, a high quality factor ($Q{\cdot}f$) for achieving prominent frequency selectivity and stability and a near zero temperature coefficient of resonant frequency (τ_f) for temperature stability [3,4]. From an empirical perspective, combining two ceramics which exhibit positive and negative τ_f respectively in a suitable proportion should yield a temperature stable material [5,6].

In the past work, $Ca(Mg_{1/3}Nb_{2/3})O_3$ dielectric ceramic was reported to be a good dielectric resonator material with $\varepsilon_r = 28$, $Q{\cdot}f = 58{,}000$ GHz [7]. But the τ_f of $Ca(Mg_{1/3}Nb_{2/3})O_3$ is a large negative value (−48 ppm/°C), which limits its practical applications. In order to compensate the τ_f of $Ca(Mg_{1/3}Nb_{2/3})O_3$, $CaTiO_3$ was added to form the $0.4CaTiO_3$–$0.6Ca(Mg_{1/3}Nb_{2/3})O_3$ solid solution which shows good microwave dielectric properties: $\varepsilon_r = 47.3$, $Q{\cdot}f = 25{,}630$ GHz and $\tau_f = +8.2$ ppm/°C [8]. However, its $Q{\cdot}f$ still needs to be promoted prior to a practical application as GPS antennas.

In the present work, $Ca_{0.6}La_{0.267}TiO_3$ ($\varepsilon_r = 109$, $Q{\cdot}f = 17{,}600$ GHz, $\tau_f = +213$ ppm/°C [9]), having a much higher $Q{\cdot}f$ value than $CaTiO_3$, was chosen as a τ_f compensator for $Ca(Mg_{1/3}Nb_{2/3})O_3$. The results indicated that not only compensation for the τ_f was achieved by employing the solid solutions of $Ca_{0.6}La_{0.267}TiO_3$–$Ca(Mg_{1/3}Nb_{2/3})O_3$ ceramics but also the $Q{\cdot}f$ value showed a promotion of more than 40% compared with the $CaTiO_3$–$Ca(Mg_{1/3}Nb_{2/3})O_3$ ceramics. In addition, X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis were employed to study the crystal structures and microstructures of the present ceramics. The relation between the microstructure and the microwave dielectric properties was also investigated.

2. Experimental procedure

The starting materials were high-purity carbonate or oxide powders (>99.9%): $CaCO_3$, La_2O_3, MgO, Nb_2O_5 and TiO_2. At first, $Ca_{0.6}La_{0.267}TiO_3$ and $Ca(Mg_{1/3}Nb_{2/3})O_3$ powders were synthesized respectively by mixing the starting materials according to the desired stoichiometry, ball milling for 8 h with

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zirconia balls, and calcined at 1050 °C for 2 h. Then the calcined powders were mixed according to the composition of $(1-x)Ca_{0.6}La_{0.267}TiO_3$–$xCa(Mg_{1/3}Nb_{2/3})O_3$ ($x = 0.4$–0.6) and then re-milled for 8 h. After being dried, the resultant mixtures were pressed to pellets with dimensions of 11 mm in diameter and 5 mm in thickness under a pressure of 300 MPa and then were sintered at 1400–1520 °C for 4 h in air. The heating rate and cooling rate were both set at 2 °C/min.

The crystalline phases of the sintered ceramics were identified by XRD using Cu Kα radiation. The microstructures of the sintered samples were observed by SEM equipped with energy dispersive spectroscope (EDS). The bulk densities of the samples were measured by the Archimedes method. The dielectric properties of the samples at microwave frequency were measured using the modified Hakki and Coleman's method, as modified and improved by Courtney [10,11]. τ_f was evaluated in a temperature range from 25 to 80 °C.

3. Results and discussion

Fig. 1 illustrates the relative densities and temperature coefficient of resonant frequency (τ_f) of $(1-x)Ca_{0.6}La_{0.267}TiO_3$–$xCa(Mg_{1/3}Nb_{2/3})O_3$ ceramic system sintered at 1490 °C for 4 h. All samples show relative densities higher than 98%, which suggests that dense ceramics with different x values can be obtained by sintering at 1490 °C for 4 h. As the x value increases from 0.4 to 0.6, the τ_f value varies from 47.1 ppm/°C to −15.7 ppm/°C. In general, τ_f is related to the phase composition of the ceramics and insensitive to the sintering temperature. The decrease in $Ca_{0.6}La_{0.267}TiO_3$ ($\tau_f = +213$) content and increase in $Ca(Mg_{1/3}Nb_{2/3})O_3$ ($\tau_f = -48$ ppm/°C) content leads to a variation of τ_f toward negative value. A near zero τ_f value can be obtained by appropriately adjusting the x value. At $x = 0.5$, a near zero τ_f value of 3.4 ppm/°C was achieved for the present ceramic system.

Fig. 2 shows the XRD patterns of $(1-x)Ca_{0.6}La_{0.267}TiO_3$–$xCa(Mg_{1/3}Nb_{2/3})O_3$ ceramics with different x values sintered at 1490 °C for 4 h. Only perovskite phases are observed for all compositions. The XRD patterns of $0.5Ca_{0.6}La_{0.267}TiO_3$–$0.5Ca(Mg_{1/3}Nb_{2/3})O_3$ (following referred to as 5CLT–5CMN) ceramics sintered at different temperatures for 4 h are shown in Fig. 3. It can be seen that sintering temperature shows little influence on the phase composition of the 5CLT–5CMN ceramics. The only perovskite phases were identified for all samples, except for an increase in peak intensity with increasing sintering temperature.

SEM micrographs of the $(1-x)Ca_{0.6}La_{0.267}TiO_3$–$xCa(Mg_{1/3}Nb_{2/3})O_3$ ceramics with different x values sintered at 1490 °C for 4 h are illustrated in Fig. 4. All images show dense microstructures with little pores, which is consistent with the relative density results. However, the grain size is not uniform, which seems insensitive to x. Fig. 5 illustrates SEM micrographs of the 5CLT–5CMN ceramics sintered at different

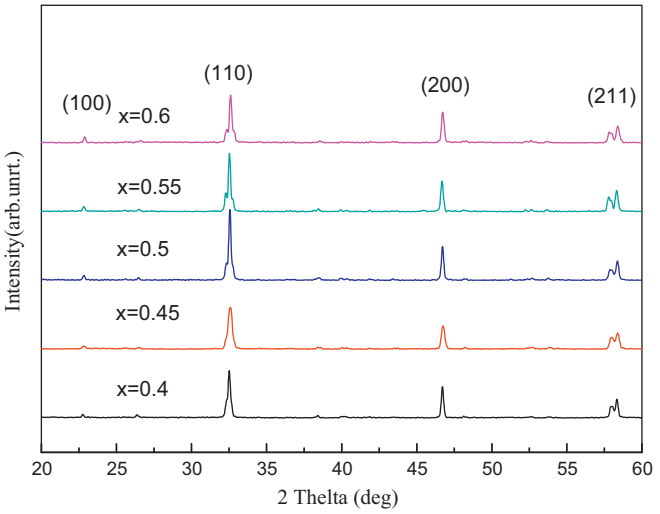

Fig. 2. XRD patterns of $(1-x)Ca_{0.6}La_{0.267}TiO_3$–$xCa(Mg_{1/3}Nb_{2/3})O_3$ ceramics with different x values sintered at 1490 °C for 4 h.

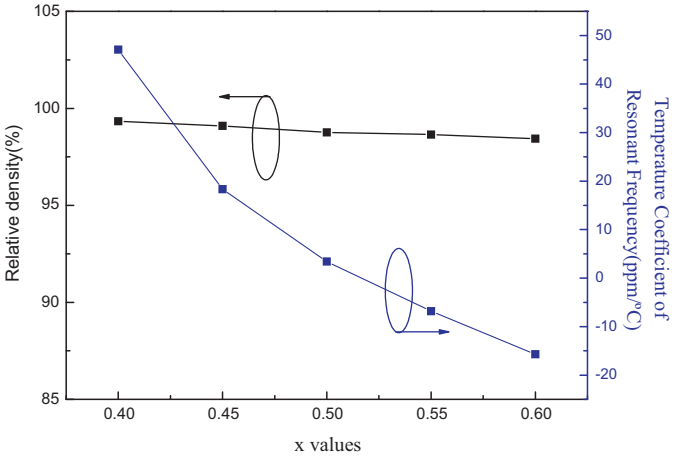

Fig. 1. Relative density and temperature coefficient of resonant frequency of $(1-x)Ca_{0.6}La_{0.267}TiO_3$–$xCa(Mg_{1/3}Nb_{2/3})O_3$ ceramic system sintered at 1490 °C for 4 h.

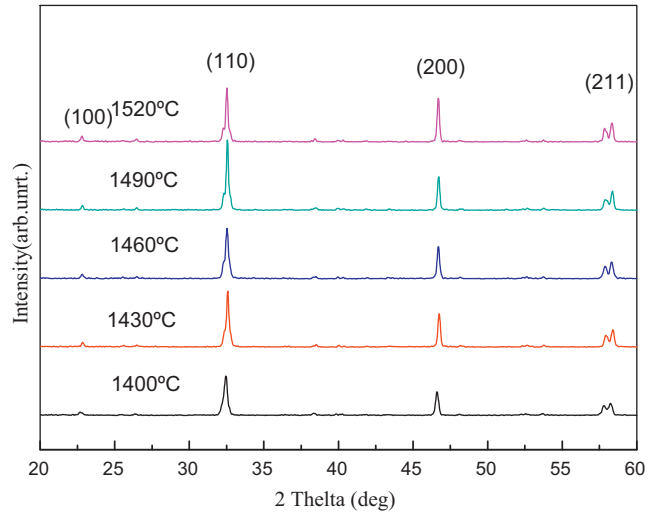

Fig. 3. XRD patterns of 5CLT–5CMN ceramics sintered at different temperatures for 4 h.

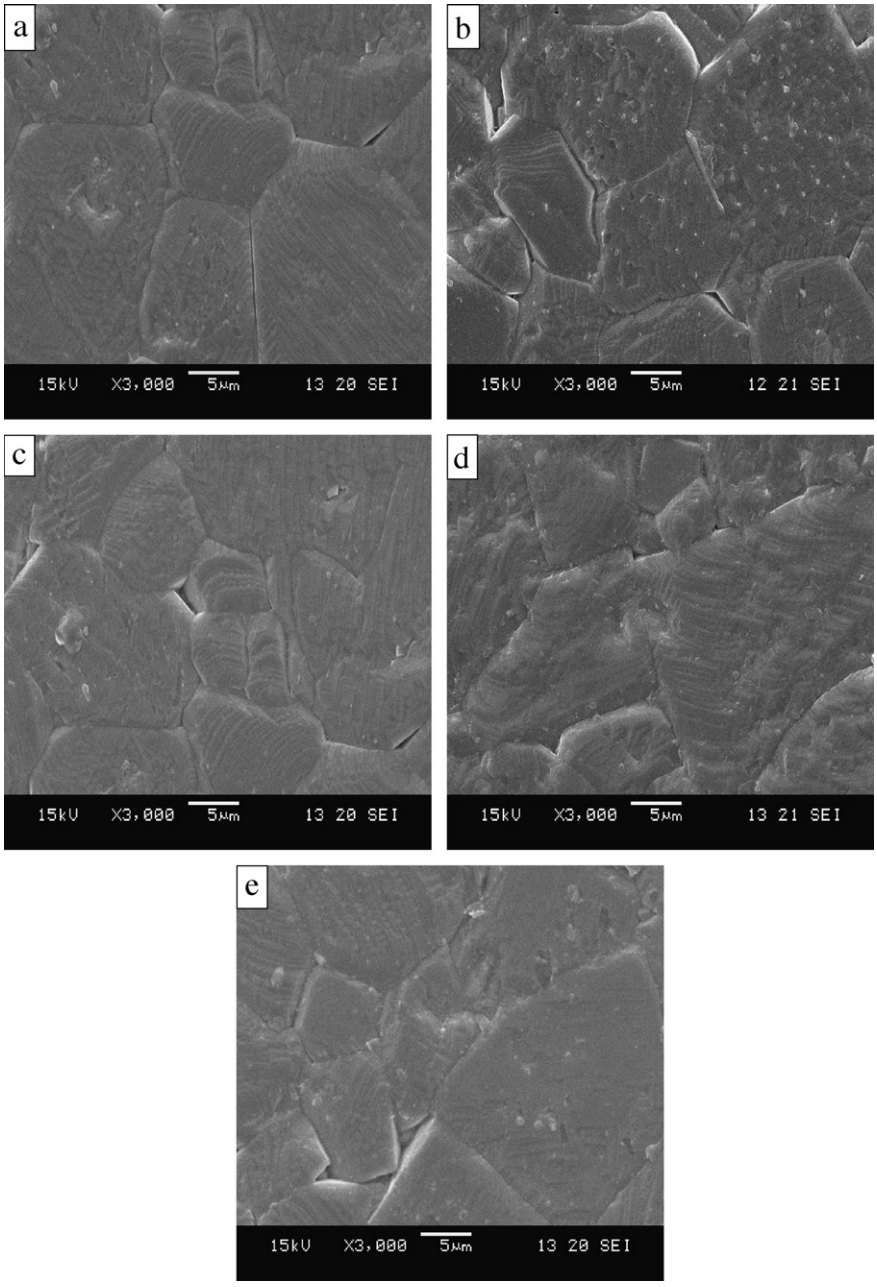

Fig. 4. SEM micrographs of the $(1-x)Ca_{0.6}La_{0.267}TiO_3$–$xCa(Mg_{1/3}Nb_{2/3})O_3$ ceramics with different x values sintered at 1490 °C for 4 h: (a) $x = 0.4$, (b) $x = 0.45$, (c) $x = 0.5$, (d) $x = 0.55$, and (e) $x = 0.6$.

temperatures for 4 h. Many small grains and a few pores are observed in the sample sintered at 1400 °C. Then with the increase of sintering temperature, pores and small grains reduce gradually. In order to further verify the formation of $(1-x)Ca_{0.6}La_{0.267}TiO_3$–$xCa(Mg_{1/3}Nb_{2/3})O_3$ solid solution, the compositions of the grains were analysed by EDS. The EDS results are shown in Fig. 5(d) and Table 1, respectively. It can be seen that these grains show nearly identical and desired

Table 1
The EDS data of the spots A–D marked in Fig. 4(d).

Spots	Atom (%)					
	Ca K	Mg K	Nb L	La L	Ti K	O K
A	15.53	3.31	7.11	2.11	8.62	63.32
B	15.88	3.27	7.49	2.16	9.06	62.14
C	15.26	3.58	6.68	2.09	9.60	62.79
D	15.58	3.24	6.91	2.36	9.26	62.65

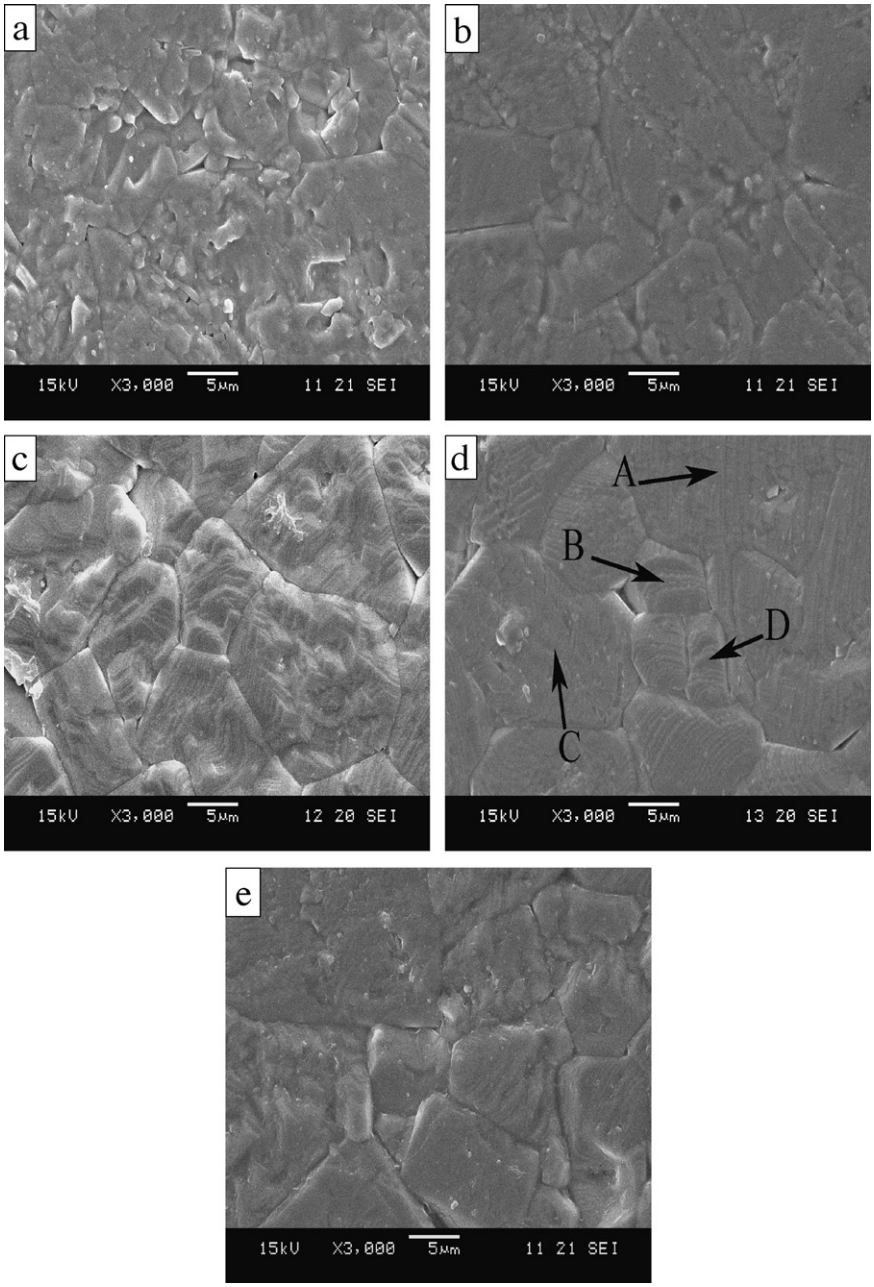

Fig. 5. SEM photographs of 5CLT–5CMN ceramics sintered at (a) 1400 °C, (b) 1430 °C, (c) 1460 °C, (d) 1490 °C, and (e) 1520 °C for 4 h.

composition, indicating that a full solid solution can be formed in the 5CLT–5CMN ceramic system.

Variations of relative density and ε_r for 5CLT–5CMN ceramics as a function of sintering temperature are shown in Fig. 6. With increasing temperature from 1400 to 1520 °C, the relative densities are always higher than 98%, implying that all the specimens are well-sintered at all sintering temperatures. The variation of ε_r is consistent with that of density. With the increase of sintering temperature and the slight decrease of density, the ε_r decreases slightly from 53.14 to 52.10.

The $Q{\cdot}f$ and τ_f values of the 5CLT–5CMN ceramics with various sintering temperatures are illustrated in Fig. 7. As shown in Fig. 7, the $Q{\cdot}f$ value increases from 26,888 to 36,428 GHz as the sintering temperature increases from 1400 to 1490 °C, then decreases to 35,479 GHz at 1520 °C. The microwave dielectric loss is mainly caused not only by the lattice vibrational modes, but also by pores, second phases, impurities and the lattice defect [12,13]. Moreover, the decrease in the amount of grain boundary can improve the $Q{\cdot}f$ value of ceramics [14]. In the present study, the increase of $Q{\cdot}f$ value may be attributed to the well-developed grain growth, as shown in Fig. 5. Since the τ_f of a material is known to be governed by the phase composition, no significant variation in the τ_f value (τ_f = 2.1–9.2 ppm/°C) for the 5CLT–5CMN ceramics is observed as a result of the little variation of phase composition with sintering temperature. Typically, the 5CLT–5CMN

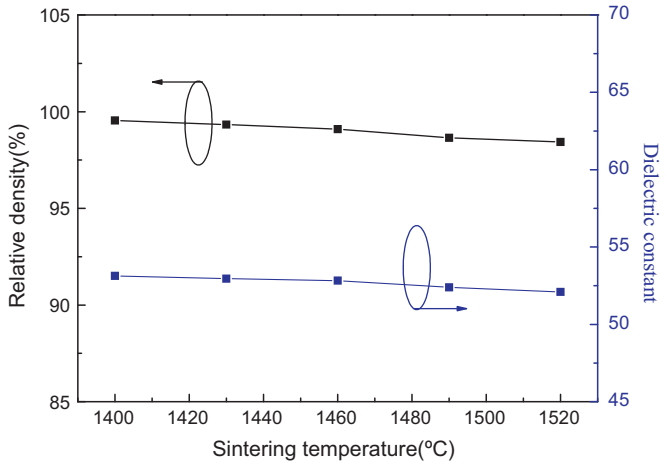

Fig. 6. Relative density and dielectric constant of 5CLT–5CMN ceramics as a function of sintering temperature.

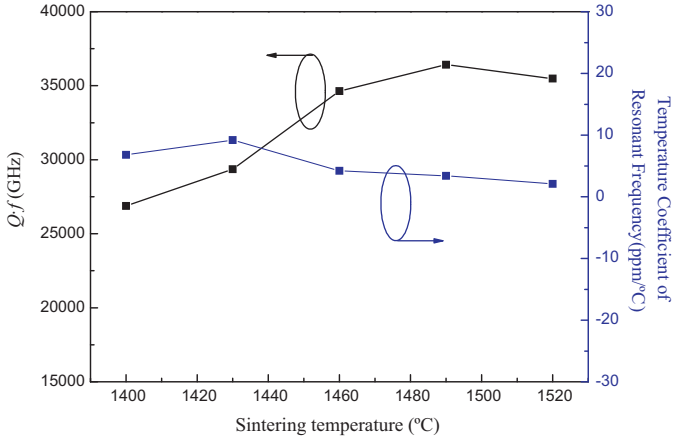

Fig. 7. $Q{\cdot}f$ and τ_f values of 5CLT–5CMN ceramics as a function of sintering temperature.

ceramics sintered at 1490 °C possess excellent microwave dielectric properties, especially the highest $Q{\cdot}f$ value ($Q{\cdot}f$ = 36,428 GHz).

4. Conclusion

The microstructure and microwave dielectric properties of $(1-x)Ca_{0.6}La_{0.267}TiO_3$–$xCa(Mg_{1/3}Nb_{2/3})O_3$ ceramics (x = 0.4–0.6) were investigated as a function of composition and sintering temperature. In all cases, the sintered ceramics had the high relative densities and exhibited pure perovskite structures. A near zero τ_f could be obtained with x = 0.5 in the ceramics system. The sintering temperature showed significant effect on the $Q{\cdot}f$ value by influencing the grain growth. However, it had no effect on ε_r and τ_f. A good combination of microwave dielectric properties (ε_r = 52.4, $Q{\cdot}f$ = 36,428 GHz and τ_f = 3.4 ppm/°C) was obtained for the $0.5Ca_{0.6}La_{0.267}TiO_3$–$0.5Ca(Mg_{1/3}Nb_{2/3})O_3$ ceramics sintered at 1490 °C for 4 h, suggesting that it could be used as a candidate material for small-sized GPS patch antennas.

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