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Microstructures and microwave dielectric properties of $(1-y)La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics

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Abstract

The $(1-y)La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics were prepared by the conventional solid-state method. The X-ray diffraction patterns of the $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics revealed that $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ is the main crystalline phase, which is accompanied by a little $La_2Sn_2O_7$ as the second phase. An apparent density of 6.59 g/cm^3, a dielectric constant (ε_r) of 19.9, a quality factor ($Q \times f$) of 70,200 GHz, and a temperature coefficient of resonant frequency (τ_f) of −77 ppm/°C were obtained when the $La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$ ceramics were sintered at 1500 °C for 4 h. The temperature coefficient of resonant frequency (τ_f) increased from −77 to +6 ppm/°C as y increased from 0 to 0.6 when the $(1-y)La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics were sintered at 1500 °C for 4 h. $0.425La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$0.575Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramic that was sintered at 1500 °C for 4 h had a τ_f of −3 ppm/ °C.

Keywords: A. Sintering; C. Dielectric properties; Ceramic; X-ray diffraction

1. Introduction

The benefits of using complex perovskite ceramics $A(B'_{0.5}B''_{0.5})O_3$ ($A = Me^{2+}$, Me^{3+}; $B' = Me^{2+}$, Me^{3+}; $B'' = Me^{4+}$, Me^{5+}, Me^{6+}) are reportedly associated with their excellent microwave dielectric properties [1–7]. Many investigations of $La(Mg_{0.5}Sn_{0.5})O_3$ ceramics and related ceramic systems have investigated their potential application in resonators, filters and antennas in modern communication systems, such as radar and wireless local area network (WLAN), which are operated at microwave frequencies. A dielectric constant of 15.6 and a $Q \times f$ of 30,600 GHz were obtained for $La(Mg_{0.5}Sn_{0.5})O_3$ ceramics, sintered at 1500 °C for 4 h [8]. A dielectric constant of 20.3, a $Q \times f$ of 48,400 GHz, and a temperature coefficient of resonant frequency of −88 ppm/°C was obtained for $La(Mg_{0.5}Sn_{0.5})O_3$ ceramics with 0.5 wt% V_2O_5 additive, sintered at 1500 °C for 4 h [9]. $La(Mg_{0.5}Sn_{0.5})O_3$ ceramics with 0.5 wt% B_2O_3 additive, sintered at 1500 °C for 4 h, have been obtained with a dielectric constant of 19.7, a $Q \times f$ of 45,000 GHz and a temperature coefficient of resonant frequency of −85 ppm/°C [10]. Several solid solutions were found to have a higher value of $Q \times f$ compared with that of both end members [11–13], this phenomenon motivates this study of the effect of the substitution of La^{3+} (0.1032 nm) by Sm^{3+} (0.0958 nm) to form $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics [14]. Combining two compounds with negative and positive temperature coefficients is the most effective means of obtaining a near-zero temperature coefficient of resonant frequency. $Ca_{0.8}Sm_{0.4/3}TiO_3$ is a good candidate to compensate the negative τ_f value of $La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$ ceramics. Since $Ca_{0.8}Sm_{0.4/3}TiO_3$ has a high dielectric constant ($\varepsilon_r = 119.3$) and a large positive temperature coefficient of resonant frequency ($\tau_f \sim +400$ ppm/°C) [15], the dielectric constant and temperature coefficient of resonant frequency of $La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$ ceramics can be improved by introducing $Ca_{0.8}Sm_{0.4/3}TiO_3$ to form the $(1-y)La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics.

In this investigation, $La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$ ceramics were synthesized and some of the La^{3+} ions were substituted by

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Sm^{3+} ions to improve their $Q \times f$. Relatively high τ_f of the $La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$ ceramics precludes its immediate application potential. An investigation involved tailoring the τ_f of $La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$ ceramics by combining $Ca_{0.8}Sm_{0.4/3}TiO_3$. The microwave dielectric properties of $(1-y)La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics were studied. The microwave dielectric properties of $(1-y)La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics were found to vary with different extents of $Ca_{0.8}Sm_{0.4/3}TiO_3$. These various microwave dielectric properties were analyzed by densification, X-ray diffractometry (XRD), and observation of their microstructures.

2. Experimental procedure

The $(1-y)La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics were prepared using the conventional solid state method. The starting raw chemicals were La_2O_3 (99.99%), Sm_2O_3 (99.9%), MgO (98.0%), SnO_2 (99.0%), $CaCO_3$ (99.9%), and TiO_2 (99.9%) powders. The purity of the MgO starting material was 98.0%, this could affect the detailed microwave dielectric properties. A later investigation will involve preparation of the compound using highly pure MgO. Such a method may yield higher values of the parameters of interest. The raw materials were mixed according to the stoichiometric proportions of $(1-y)La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics. The powders were ball-milled in alcohol for 12 h and dried. The $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ and $Ca_{0.8}Sm_{0.4/3}TiO_3$ were then calcined at 1200 °C for 4 h. The calcined powders were mixed to the $(1-y)La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics with the desired composition and remilled for 12 h. The obtained powders were then crushed into fine particles using a sieve with a 200 mesh. The powder thus obtained was then axially pressed at 2000 kg/cm^2 into pellets with a diameter of 11 mm and a thickness of 6 mm. These specimens were then sintered at 1500 °C for 4 h. Both the heating rate and the cooling rate were set at 10 °C/min.

Following sintering, the phases of the samples were investigated by X-ray diffraction. An X-ray Rigaku D/MAX-2200 with Cu Kα radiation (at 30 kV and 20 mA) was utilized and a graphite monochromator in the 2θ range of 20–80°. Scanning electron microscopy (SEM; JEOL JSM-6500F) and energy dispersive spectroscopy (EDS) were carried out to examine the microstructures of the specimens. The apparent densities of the specimens were measured using the liquid Archimedes method using distilled water. The microwave dielectric properties of the specimens were measured by the postresonator method that was developed by Hakki and Coleman [16]. This method employs a specimen in the form of a cylinder of diameter D and length L. The specimens whose microwave dielectric property were measured had an aspect ratio D/L of approximately 1.6, which is in the permitted range that was determined by Kobayashi and Katoh [17]. The cylindrical resonator was sandwiched between two conducting plates. Two small antennas were positioned in the vicinity of the specimen to couple the microwave signal power into or out of the resonator. The other ends of the antennas were connected to an Agilent E5071C network analyzer. The resonance characteristics depended on the size and the microwave dielectric properties of the specimen. The microwave energy was coupled using electric-field probes. The TE_{011} resonant mode was optimal for determining the dielectric constant and the loss factor of the specimen. The Agilent E5071C network analyzer was adopted to identify the TE_{011} resonant frequency of the dielectric resonator, and the dielectric constant and quality factor were calculated. The approach for measuring τ_f was the same as that adopted for measuring the dielectric constant. The test cavity was placed in a chamber and the temperature increased from 25 to 75 °C. The τ_f value (ppm/°C) was determined from the change in resonant frequency [18]:

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

where f_1 and f_2 denote the resonant frequencies at T_1 and T_2, respectively.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics with x varied from 0 to 0.05, following sintering at 1500 °C for 4 h. Clearly, $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ is the main crystalline phase, which is accompanied by small amounts of $La_2Sn_2O_7$ as the second phase. $La_2Sn_2O_7$ with a cubic crystal structure (ICDD-PDF #73-1686) was identified and difficult to eliminate completely from the sample that was prepared by the mixed oxide route. A later investigation will involve preparation of the powder by precipitation from solution. This method may yield a single-phase product. A single-phase product potentially has much higher values of the parameters of interest. As shown in Fig. 1, the (2 2 2), (4 0 0), and (6 2 2) peaks of the $La_2Sn_2O_7$ ceramics were at 28.880°, 33.470°, and 57.044°, respectively. A series of extra peaks were observed to correspond to superlattice reflections. All of the superlattice reflections were indexed using half-integer Miller indices. According to Glazer, the superlattice reflections, with specific combinations of odd (o) and even (e) Miller indices, revealed particular deviations of the structure from the undistorted cubic structure, such as

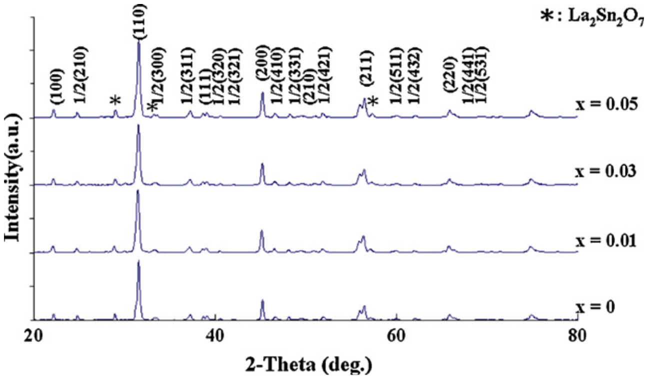


Fig. 1. X-ray diffraction patterns of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ specimens sintered at 1500 °C for 4 h with x varied from 0 to 0.05.

Table 1
Tolerance factor, main phase (%) and second phase (%) of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics.

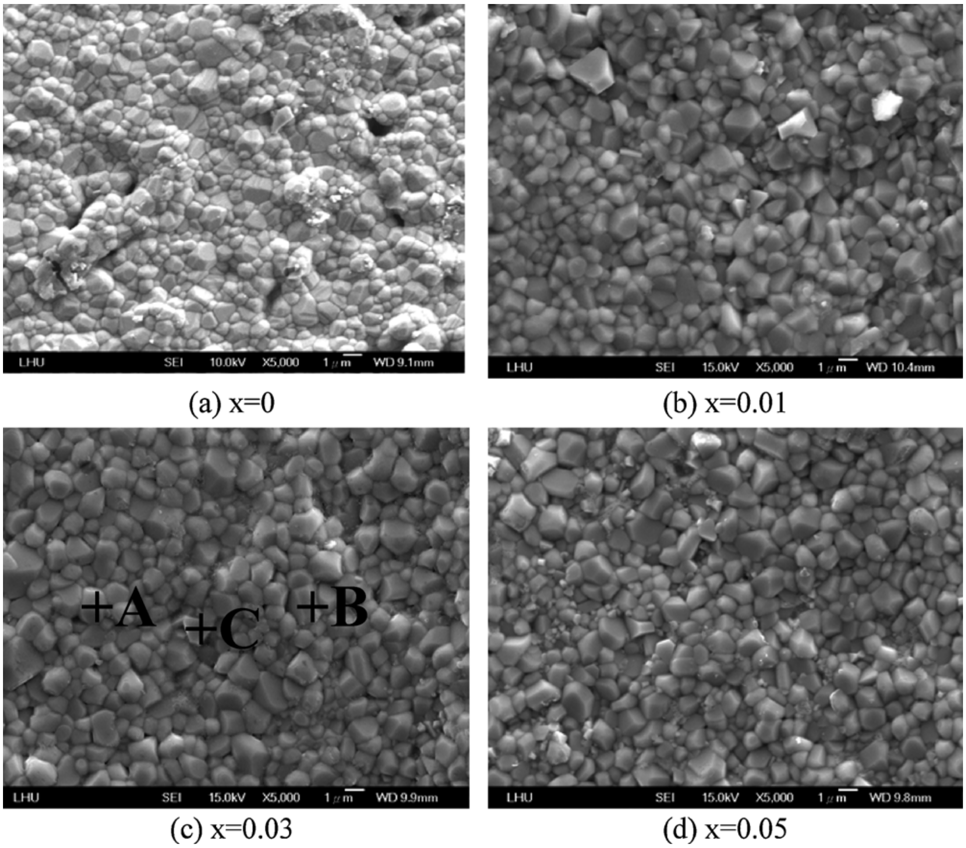
x	Tolerance factor	Main phase (%)	Second phase (%)
0	0.9138	90.09	9.91
0.01	0.9125	90.13	9.87
0.03	0.9101	90.89	9.11
0.05	0.9076	90.94	9.06

octahedral in-phase tilting (ooe, oeo, eoo), anti-phase tilting (ooo, $h + k + l > 3$), and the anti-parallel displacement of A-cations (eeo, eoe, oee) [19]. The (1/2(2 1 0), 1/2(3 0 0), 1/2(3 2 0), 1/2 (4 1 0), 1/2(4 2 1), 1/2(4 3 2), and 2(4 4 1)) extra peaks indicated the anti-parallel displacement of A-cations; the (1/2(3 1 1), 1/2(3 3 1), and 1/2(5 1 1)) peaks revealed anti-phase tilting, and the 1/2(3 2 1) peaks indicated in-phase tilting. The tolerance factors of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics decreased from 0.9138 to 0.9076 as x increased from 0 to 0.05, as presented in Table 1. The tolerance factor was calculated using the ionic radius data of Shannon [14]. The tolerance factors of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ series are in the anti-phase and in-phase titled region [20], which result is in agreement with the X-ray diffraction patterns, as described above. The perovskite cell deformed when tolerance factor deviated from one. Deviation from cubic symmetry resulted in extra polarizations, which reflected in the dielectric constant, and, therefore, a higher dielectric constant [21]. The amount of main phase was evaluated from most intense lines of the main and second phases:

$$La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3\ (\text{vol}\%) = \frac{I_{A(1\,1\,0)}}{I_{A(1\,1\,0)} + I_{B(2\,2\,2)}} \times 100, \tag{2}$$

where I_A and I_B denote the largest intensities of the lines from $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ (1 1 0) and $La_2Sn_2O_7$ (2 2 2), respectively. Table 1 shows the proportions of the main phase of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics increased from 90.09% to 90.94% as x increased from 0 to 0.05. The proportion of second phase in specimens was lowest when x was 0.05. The formation of the second phase, $La_2Sn_2O_7$ affected the apparent density and microwave dielectric properties of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics.

Fig. 2 shows the microstructures of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics, following sintering for 4 h at 1500 °C. Comparing the microstructures of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics that were sintered at 1500 °C for 4 h indicated $La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$ ceramics had a maximum grain size in the series of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics. To indentify the composition of the second phase, an energy-dispersive spectroscopy (EDS) was conducted on the grains of $La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$ ceramics that were sintered at 1500 °C for 4 h, as displayed in Fig. 2(c). According to the quantitative analysis, as shown in



(a) x=0 (b) x=0.01

(c) x=0.03 (d) x=0.05

Fig. 2. Microstructures of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics with various degrees of Sm^{3+} substitution, following sintering at 1500 °C for 4 h: (a) $x = 0$, (b) $x = 0.01$, (c) $x = 0.03$, and (d) $x = 0.05$.

Table 2
EDS data f grains of $La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$ ceramics sintered at 1500 °C for 4 h.

Spot	La (%)	Sm (%)	Mg (%)	Sn (%)	O (%)
A	19.15	0.54	8.11	9.08	63.12
B	17.24	0.61	8.34	9.47	64.34
C	12.91	0	0	13.41	73.69

Table 2, the A and B grains are $La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$ and the grain C is $La_2Sn_2O_7$.

Fig. 3 shows the apparent densities and relative densities of the $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics with different degrees of Sm^{3+} substitution, following sintering at 1500 °C for 4 h. The apparent density increased significantly from 6.19 to 6.59 g/cm^3 as x increased from 0 to 0.01 and increased slightly from 6.59 to 6.61 g/cm^3 as x increased from 0.01 to 0.05. The density of the composites can be calculated using the equation:

$$D_{\mathrm{composite}} = v_1 D_1 + v_2 D_2, \tag{3}$$

where $D_{\mathrm{composite}}$ is the density of the composite; v_1 and v_2 are the volume fractions of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ and $La_2Sn_2O_7$, respectively, and D_1 and D_2 are the densities of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ and $La_2Sn_2O_7$, respectively. The theoretical densities of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ and $La_2Sn_2O_7$ are 6.631 and 6.799 g/cm^3, respectively. Although the amount of second phase decreased as x increased from 0 to 0.05, as shown in Table 1, the apparent density of the composites increased as x increased. The increase in apparent density was associated with the fact that the weight of the Sm atom is larger than that of the La atom. The relative density of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics increased significantly from 93.1% to 99.1% as x increased from 0 to 0.01. The 6.0% difference of relative density between $La(Mg_{0.5}Sn_{0.5})O_3$ and $La_{0.99}Sm_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics was inferred to be the poor sintering for $La(Mg_{0.5}Sn_{0.5})O_3$ ceramics that were sintered at 1500 °C for 4 h.

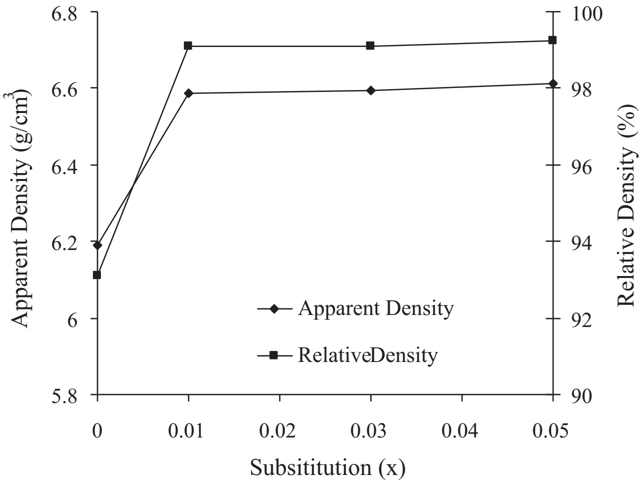


Fig. 3. Apparent densities and relative density of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics with various degrees of Sm^{3+} substitution, following sintering at 1500 °C for 4 h.

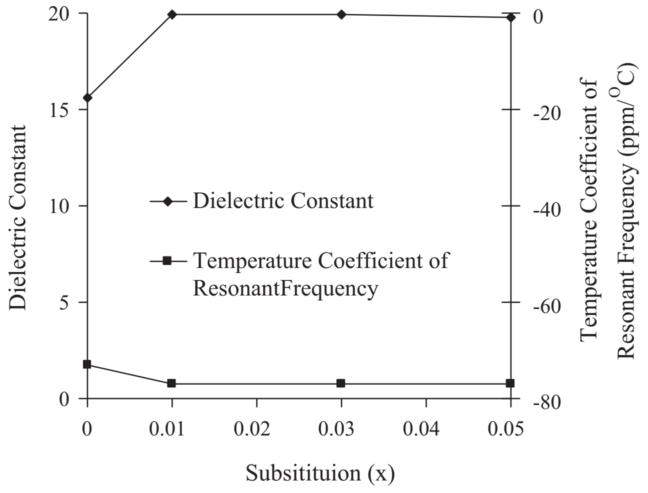


Fig. 4. Dielectric constants and τ_f of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics with various degrees of Sm^{3+} substitution, following sintering at 1500 °C for 4 h.

Fig. 4 shows the dielectric constants and temperature coefficient of resonant frequency (τ_f) of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ $)O_3$ ceramics with different degrees of Sm^{3+} substitution, following sintering at 1500 °C for 4 h. The dielectric constant of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics increased from 15.6 to 19.9 as x increased from 0 to 0.01, then stabled as x increased from 0.01 to 0.05. The significant increase in the dielectric constant of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics as x increased from 0 to 0.01 was associated with the relative density. The dielectric constant of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics is affected by many factors, included ionic polarization, tolerance factor, and second phase. In the cases of ionic polarization, as suggested by Tohdo et al., the dielectric constant can be calculated using the Clausius–Mossotti equation [22]:

$$\varepsilon_r = \frac{3V_m + 8\pi\alpha_D}{3V_m - 4\pi\alpha_D} \tag{4}$$

where V_m represents the molar volume and α_D is the sum of the ionic polarizabilities of individual ions. The dielectric constant calculated using Eq. (4) was intrinsic factor to dielectric property. Dielectric constants therefore depend on the molar volume and ionic polarization. As indicated by Eq. (4), a smaller molar volume or a larger ionic polarization is associated with a larger dielectric constant. The influence of ionic polarization on dielectric constant is much larger than that of molar volume. The ionic polarizations of La^{3+} and Sm^{3+} ions are 4.82 and 4.74 Å^3, respectively [23,24]. The sum of ionic polarizations of the individual ions of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics decreased as x increased, so the dielectric constant of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics is inferred to decrease with x. However, the dielectric constant of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O^3$ ceramics stabled as x increased from 0.01 to 0.05. This fact may be explained by the second phase. The second phase is extrinsic factor in controlling the dielectric constant. A dielectric constant of 14.3 was obtained for $La_2Sn_2O_7$ ceramic, as presented

Table 3
Microwave dielectric properties of $La_2Sn_2O_7$ ceramics sintered at 1550 °C for 34 h.

ε_r	$Q \times f$ (GHz)	τ_f (ppm/ °C)
14.3	38,300	−53

in Table 3. The dielectric constant of the composite can be calculated using the mixture rule:

$$\log \varepsilon_r = v_1 \log \varepsilon_{r1} + v_2 \log \varepsilon_{r2}, \quad (5)$$

where ε_r is the dielectric constant of the composite; v_1 and v_2 are the volume fractions of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ and $La_2Sn_2O_7$, respectively, and ε_{r1} and ε_{r2} are the dielectric constants of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ and $La_2Sn_2O_7$, respectively. Since the amount of the second phase decreased from 9.91% to 9.06% as x increased from 0 to 0.05, the dielectric constants of the specimens is inferred to have increased as x increased. Generally, τ_f is related to the composition and the amount of second phase that is present in ceramics. $La_2Sn_2O_7$ ceramics exhibited a τ_f of −53 ppm/°C, as presented in Table 3. The τ_f of $La_2Sn_2O_7$ ceramics is less negative compared with that of the $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics, implying that the presence of the second phase made the τ_f of the specimen positive. A τ_f of −77 ppm/°C was measured for the $La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$ ceramics that were sintered at 1500 °C for 4 h.

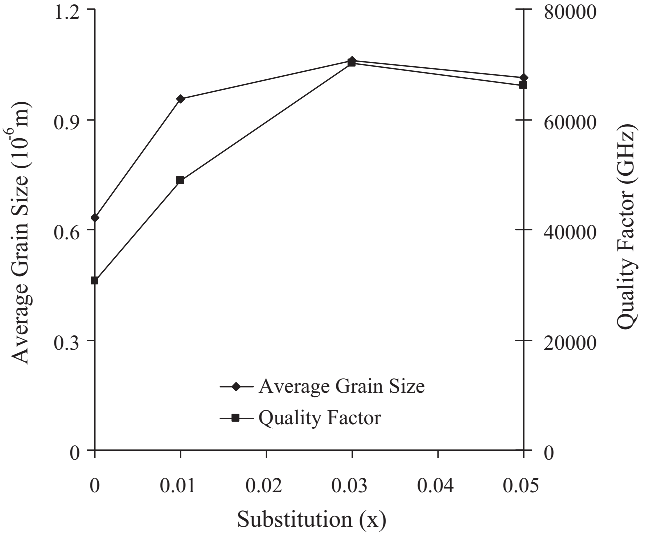
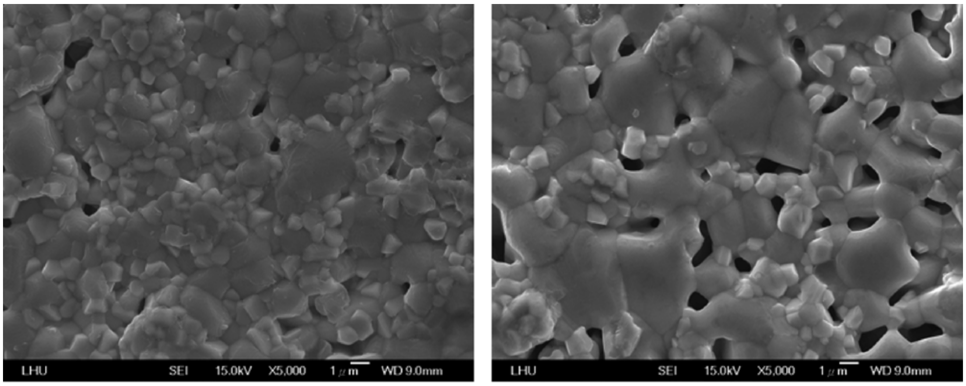
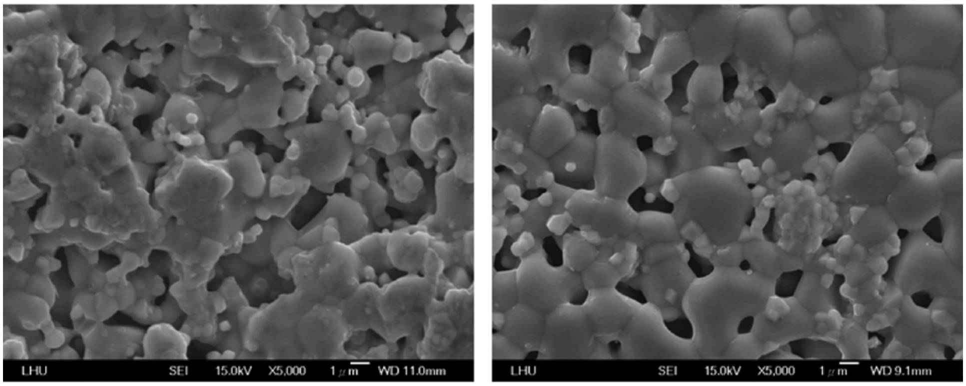


Fig. 5. $Q \times f$ and average grain sizes of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics with various degrees of Sm^{3+} substitution, following sintering at 1500 °C for 4 h.

Fig. 5 shows the $Q \times f$ and average grain sizes of the $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics with different degrees of Sm^{3+} substitution, following sintering at 1500 °C for 4 h. $La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$ ceramics had a maximum $Q \times f$ of 70,200 GHz. The results suggest that partially substituting La^{3+}



(a) y=0.5 (b) y=0.55



(c) y=0.575 (d) y=0.6

Fig. 6. Microstructures of the $(1-y)La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics that were sintered at 1500 °C for 4 h: (a) $y = 0.5$, (b) $y = 0.55$, (c) $y = 0.575$, (d) $y = 0.6$.

ions with Sm^{3+} ions increased the $Q \times f$. A $Q \times f$ of 38,300 GHz was obtained for $La_2Sn_2O_7$ ceramics, as presented in Table 3. Since the proportion of second phase decreased from 9.91% to 9.06% as x increased from 0 to 0.05, the $Q \times f$ of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics is inferred to increase with x. However, the $Q \times f$ decreased as x increased from 0.03 to 0.05. The $Q \times f$ increased with x when $x \leq 0.03$, then decreased with x when $x > 0.03$ may be explained by grain size. $La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$ ceramics had a maximum grain size of 1.06 μm.

Fig. 6 presents the microstructures of $(1-y)La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics, following sintering at 1500 °C for 4 h. The $(1-y)La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics were not dense upon sintering at 1500 °C for 4 h, potentially degrading the microwave dielectric properties of the ceramic systems. The number of pores increased as y increased. The ceramics were not well-sintered and the sintering condition was not optimal. Studying the effect of sintering temperature on the microstructures and microwave dielectric properties of $(1-y)La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics will be involved in our future work.

Fig. 7 shows the apparent densities and porosities of the $(1-y)La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics. The apparent densities of the $(1-y)La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics decreased as y increased. The density of the $(1-y)La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics can be calculated using Eq. (3). Since the theoretical densities of $La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$ and $Ca_{0.8}Sm_{0.4/3}TiO_3$ are 6.64 and 4.42 g/cm^3, respectively, the apparent densities is inferred to decrease as y increased. The porosities of $(1-y)La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics increased from 0.51% to 24.66% as y increased from 0 to 0.6. The high porosities of $(1-y)La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics, which can be confirmed with those of microstructures, as presented in Fig. 6.

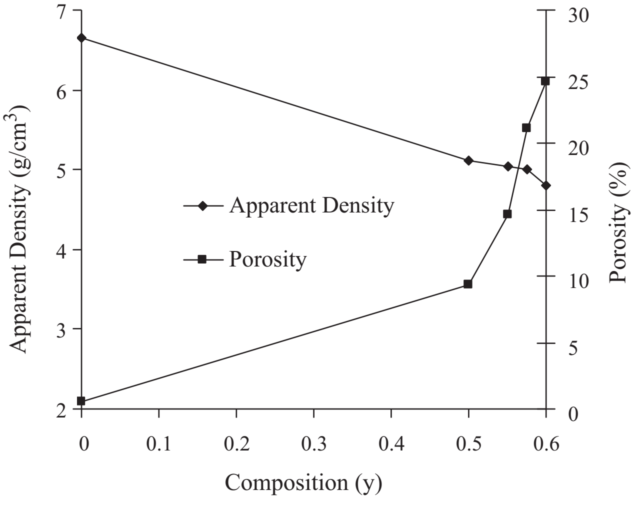


Fig. 7. Apparent densities and relative densities of $(1-y)La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics that were sintered at 1500 °C for 4 h.

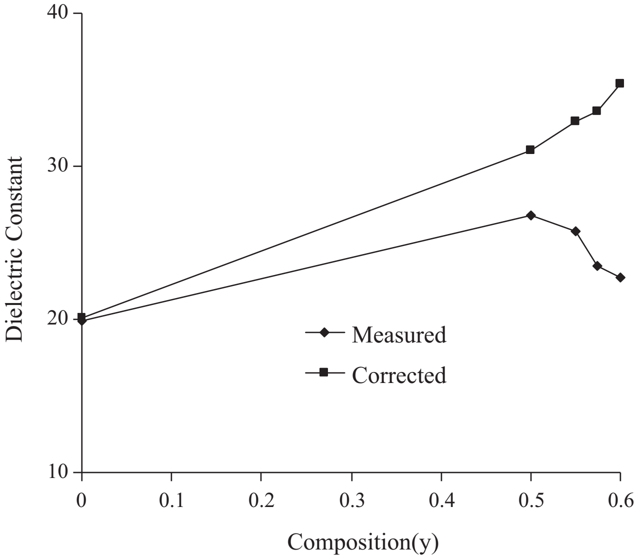


Fig. 8. Measured and corrected dielectric constants of $(1-y)La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics that were sintered at 1500 °C for 4 h.

Fig. 8 shows the measured and corrected dielectric constants of $(1-y)La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics. The corrected dielectric constant of $(1-y)La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics is calculated using following equation [25]:

$$\varepsilon_{\text{measured}} = \varepsilon_{\text{corrected}}\left(1 - \frac{3P(\varepsilon_{\text{corrected}} - 1)}{2\varepsilon_{\text{corrected}} + 1}\right), \tag{6}$$

where $\varepsilon_{\text{measured}}$ and $\varepsilon_{\text{corrected}}$ are the measured and corrected dielectric constants of the composites, respectively, and P is the fractional porosity. The corrected dielectric constant increased from 20.1 to 35.4 as y increased from 0 to 0.6. Since the dielectric constant of $Ca_{0.8}Sm_{0.4/3}TiO_3$ is 119.3 [15], which is larger than that of $La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$, the corrected dielectric constant is expected to increase as y increased.

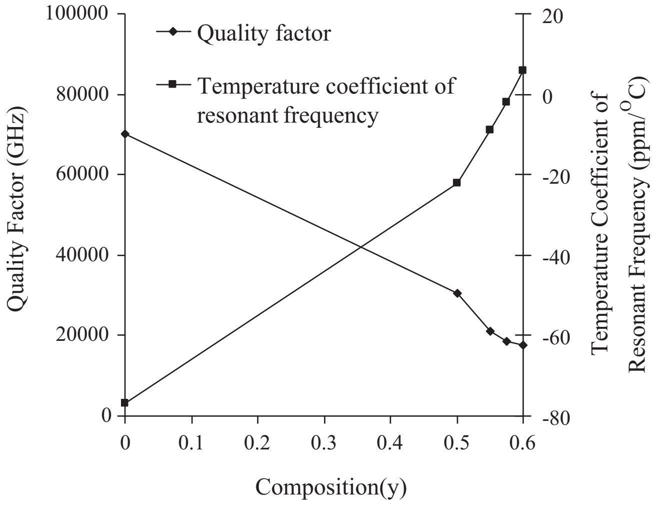


Fig. 9. $Q \times f$ and τ_f of $(1-y)La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics that were sintered at 1500 °C for 4 h.

Fig. 9 shows the $Q \times f$ and τ_f of $(1-y)La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics. The $Q \times f$ decreased nonlinearity from 70,200 to 17,700 GHz as y increased from 0 to 0.6. Since the $Q \times f$ of $La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$ is much higher than that of $Ca_{0.8}Sm_{0.4/3}TiO_3$ [15], the $Q \times f$ is expected to decrease as y increased. The τ_f increased from −77 to +6 ppm/°C as y increased from 0 to 0.6. This implies that $\tau_f = 0$ ppm/°C can be obtained by tuning the $Ca_{0.8}Sm_{0.4/3}TiO_3$ composition (y). The $0.425La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$0.575Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramic that was sintered at 1500 °C for 4 h had a measured τ_f of −3 ppm/°C. The τ_f of composite was proved to follow the empirical relationship as [26]:

$$\frac{1}{\tau_f(y)} = \frac{(1-y)\varepsilon_{r2} + y\varepsilon_{r1}}{(1-y)\varepsilon_{r2}\tau_1 + y\varepsilon_{r1}\tau_2}, \tag{7}$$

where $\tau_f(y)$ is the calculated τ_f of the composite, ε_{r1}, τ_1 and ε_{r2}, τ_2 represent the dielectric constants and τ_f of the end members. A τ_f of 0 ppm/°C was obtained when $y = 0.54$, calculated using Eq. (7). The calculated y value for τ_f of 0 ppm/°C was close to the measured result.

4. Conclusions

The effect of the degree of Sm^{3+} substitution on the microwave dielectric properties of $La_{1-x}Sm_x(Mg_{0.5}Sn_{0.5})O_3$ ceramics were studied. $La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$ ceramics that were sintered at 1500 °C for 4 h had a dielectric constant of 19.9, a $Q \times f$ of 70,200 GHz, and a τ_f of −77 ppm/°C. The dielectric constant of $La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$ ceramics was affected by the density, ionic polarization, and the amount of second phase. The $Q \times f$ of $La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$ ceramics depended on the amount of second phase and grain size. The microwave dielectric properties of $(1-y)La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics was mainly controlled by the $Ca_{0.8}Sm_{0.4/3}TiO_3$ composition (y). The τ_f of $(1-y)La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$yCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics could be tailored by controlling the $Ca_{0.8}Sm_{0.4/3}TiO_3$ composition (y). A near-zero τ_f of −3 ppm/°C was obtained for $0.425La_{0.97}Sm_{0.03}(Mg_{0.5}Sn_{0.5})O_3$–$0.575Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramic that was sintered at 1500 °C for 4 h.

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