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Elucidating the dielectric properties of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics at microwave frequencies

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The microwave dielectric properties of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics were examined with a view to their exploitation for mobile communication. The $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics were prepared by the conventional solid-state method with various sintering temperatures. The X-ray diffraction patterns of the $La(Mg_{0.5}Sn_{0.45}Ti_{0.05})O_3$ ceramics revealed no significant variation of phase with sintering temperatures. The $La_2Sn_2O_7$ intensity of the second phase of the $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics was lowest when x was 0.05. An apparent density of 6.53 g/cm^3, a dielectric constant (ε_r) of 20.8, a quality factor ($Q \times f$) of 50,100 GHz, and a temperature coefficient of resonant frequency (τ_f) of -71 ppm/^{O}C were obtained for $La(Mg_{0.5}Sn_{0.45}Ti_{0.05})O_3$ ceramics that were sintered at 1550 ^{O}C for 4 h.

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Keywords: $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$, X-ray diffraction pattern, Dielectric constant, Quality factor, Temperature coefficient of resonant frequency

1. Introduction

Various modern communication systems, including mobile radio and wireless communications, use resonators, filters, and antennas. However, these microwave devices have a limited range of sizes, gain, efficiency, and temperature stability, which are imposed by the microwave dielectric material. Microwave dielectric materials that are to be used in microwave devices must have desirable dielectric properties - a high dielectric constant (ε_r), a high quality factor ($Q \times f$), and a near-zero temperature coefficient of resonant frequency (τ_f), which enable small size, low loss, and high temperature stability, respectively [1-2].

The advantages 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 dielectric properties at microwave frequencies [3-5]. 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 that were sintered at 1500 ^{O}C for 4 h [6]. A liquid phase flux such as B_2O_3 and CuO was added to lower the sintering temperature of $La(Mg_{0.5}Sn_{0.5})O_3$ ceramics. A dielectric constant of 19.7 and a $Q \times f$ of 43,300 GHz were obtained for $La(Mg_{0.5}Sn_{0.5})O_3$ ceramics with 0.5 wt% CuO additive sintered at 1550 ^{O}C for 4 h [7]. Additionally, the temperature coefficient of resonant frequency increased from -18 to +8 ppm/K for $(1-x)La(Mg_{0.5}Sn_{0.5})O_3$-$x(Sr_{0.8}Ca_{0.2})_3Ti_2O_7$ ceramics system as the x value increased from 0.2 to 0.4 sintered at 1550 ^{O}C for 4 h [8]. Since the ionic radius of Sn^{4+} (0.069 nm) is similar to that of Ti^{4+} (0.0605 nm), the Sn^{4+} ion can be substituted with the Ti^{4+} ion to form $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ [9]. In this paper, $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ were synthesized and some of the Sn^{4+} ions were substituted with Ti^{4+} ions to improve their microwave dielectric properties. Moreover, the effect of the sintering temperature on the microwave dielectric properties of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics was studied. $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics were synthesized herein by the conventional mixed-oxide method and demonstrated to have better microwave dielectric properties than $La(Mg_{0.5}Sn_{0.5})O_3$ ceramics. The microwave dielectric properties of the $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics were found to vary with the degree of Ti^{4+} substitution and sintering temperatures. These various microwave dielectric properties were analyzed by densification, X-ray diffraction (XRD) patterns, and observation of their microstructures.

2. Experimental procedures

The starting raw chemicals were high-purity La_2O_3 (99.99%), MgO (98.0%), SnO_2 (99.0%), and TiO_2 (99.9%) powders. The prepared composition was $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$. Specimens were prepared using the conventional mixed-oxide method. The starting materials were stoichiometrically weighed after drying La_2O_3 at 1000 °C for 4 h to remove moisture content. The raw material was ball-milled in alcohol for 12 h, dried, and then calcined at 1200 ^{O}C for 4 h. The calcined powder was re-milled for 12 h using PVA solution as a binder. The obtained fine powder was then crushed into

a finer powder through a sieve with a 200 mesh. The obtained fine powder was then axially pressed at 2000 kg/cm^2 into pellets with a diameter of 11 mm and a thickness of 6 mm. The specimens thus obtained were then sintered at temperatures of 1450 to 1600 ^{O}C for 4 h in air. Both the heating rate and the cooling rate were set to 10 ^{O}C /min.

After sintering, the phases of the samples were investigated by X-ray diffraction. An X-ray Rigaku D/MAX-2200 was used with Cu$K\alpha$ radiation (at 30 KV and 20 mA) and a graphite monochromator in the 2θ range of 20^o-80^o. The microstructural observation and analysis of sintered surface were performed using a scanning electron microscope (SEM; JEOL JSM-6500F, Japan) and an energy-dispersion spectroscopy (EDS) operating at 10 kV. Before SEM observation, thin gold film was deposited on the sample surface. The apparent densities of the specimens were measured by the liquid Archimedes method using distilled water as the liquid. The microwave dielectric properties of the specimens were measured by the postresonator method that was developed by Hakki and Coleman [10]. The postresonator method employed a specimen in the form of a cylinder of diameter D and length L. The specimens used for making microwave dielectric property measurements had an aspect ratio D/L of about 1.6, which is in the permitted range determined by Kobayashi and Katoh [11]. 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 microwave dielectric properties of the specimen. The microwave energy was coupled using electric-field probes. The TE_{011} resonant mode was optimal for obtaining the dielectric constant and the loss factor of the specimen. The Agilent E5071C network analyzer was used to identify the TE_{011} resonant frequency of the dielectric resonator, and the dielectric constant and quality factor were calculated. The technique for measuring τ_f was the same as that for measuring the dielectric constant. The test cavity was placed in a chamber and the temperature was increased from 25 to 75 ^{O}C. The τ_f value (ppm/^{O}C) can be determined by noting the change in resonant frequency,

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

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 X-ray diffraction patterns of $La(Mg_{0.5}Sn_{0.45}Ti_{0.05})O_3$ ceramics that were sintered at 1450-1600 ^{O}C for 4 h. Clearly, $La(Mg_{0.5}Sn_{0.45}Ti_{0.05})O_3$ is the main crystalline phase, which is accompanied by small amounts of $La_2Sn_2O_7$ as the second phases. All of the peaks were indexed based on the cubic perovskite unit cell. A series of extra peaks were observed to correspond to superlattice reflections. All of the superlattice reflections were indexed using half-integer Miller indices. The X-ray diffraction patterns of the $La(Mg_{0.5}Sn_{0.45}Ti_{0.05})O_3$ ceramics do not significantly vary with sintering temperature. Figure 2 shows the X-ray diffraction patterns of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics as x is varied from 0.025 to 0.1, following sintering at 1550 ^{O}C for 4h. The $La_2Sn_2O_7$ intensity of the second phase of the $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics was lowest when x was 0.05. The formation of second phases of $La_2Sn_2O_7$ might affect the microwave dielectric properties of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics.

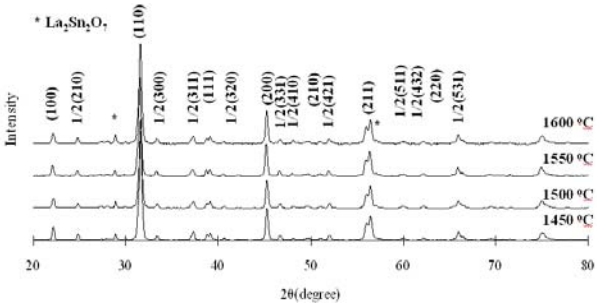

Fig. 1. X-ray diffraction patterns of $La(Mg_{0.5}Sn_{0.45}Ti_{0.05})O_3$ specimens sintered at 1450-1600 ^{O}C for 4 h.

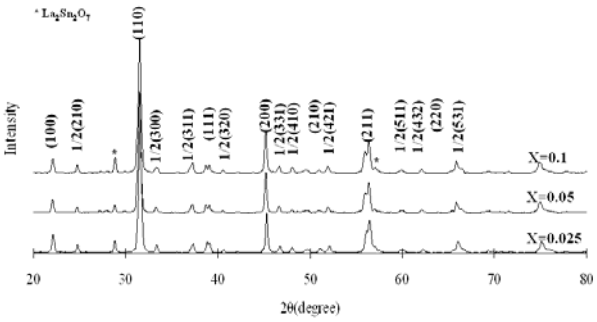

Fig. 2 X-ray diffraction patterns of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics sintered at 1550 ^{O}C for 4h.

Fig. 3 shows the microstructures of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ceramics following sintering for 4 h at different temperatures. The microstructures of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics when Sn^{4+} ions were replaced with different degrees of Ti^{4+} substitution indicated that the average grain size did not vary significantly with the extent of Ti^{4+} substitution. Comparing the microstructures of $La(Mg_{0.5}Sn_{0.475}Ti_{0.025})O_3$ ceramics that were sintered under different temperatures indicated that the average grain size increased with the sintering temperature. However, the average grain size did not considerably affect on the microwave dielectric properties of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics. The effect

of grain size on the dielectric constant and dielectric loss of dense samples can be neglected [12]. The pores of $La(Mg_{0.5}Sn_{0.475}Ti_{0.025})O_3$ ceramics almost disappeared upon sintering at 1500 ^{O}C for 4 h. To identify the composition of the second phase, energy-dispersion spectroscopy (EDS) analysis was carried out on the grains of $La(Mg_{0.5}Sn_{0.475}Ti_{0.025})O_3$ ceramics that were sintered at 1550 ^{o}C for 4 h, as shown in Fig. 4. According to the quantitative analysis, as shown in Table I, the A and B grains are $La(Mg_{0.5}Sn_{0.475}Ti_{0.025})O_3$, and the C grain is $La_2Sn_2O_7$.

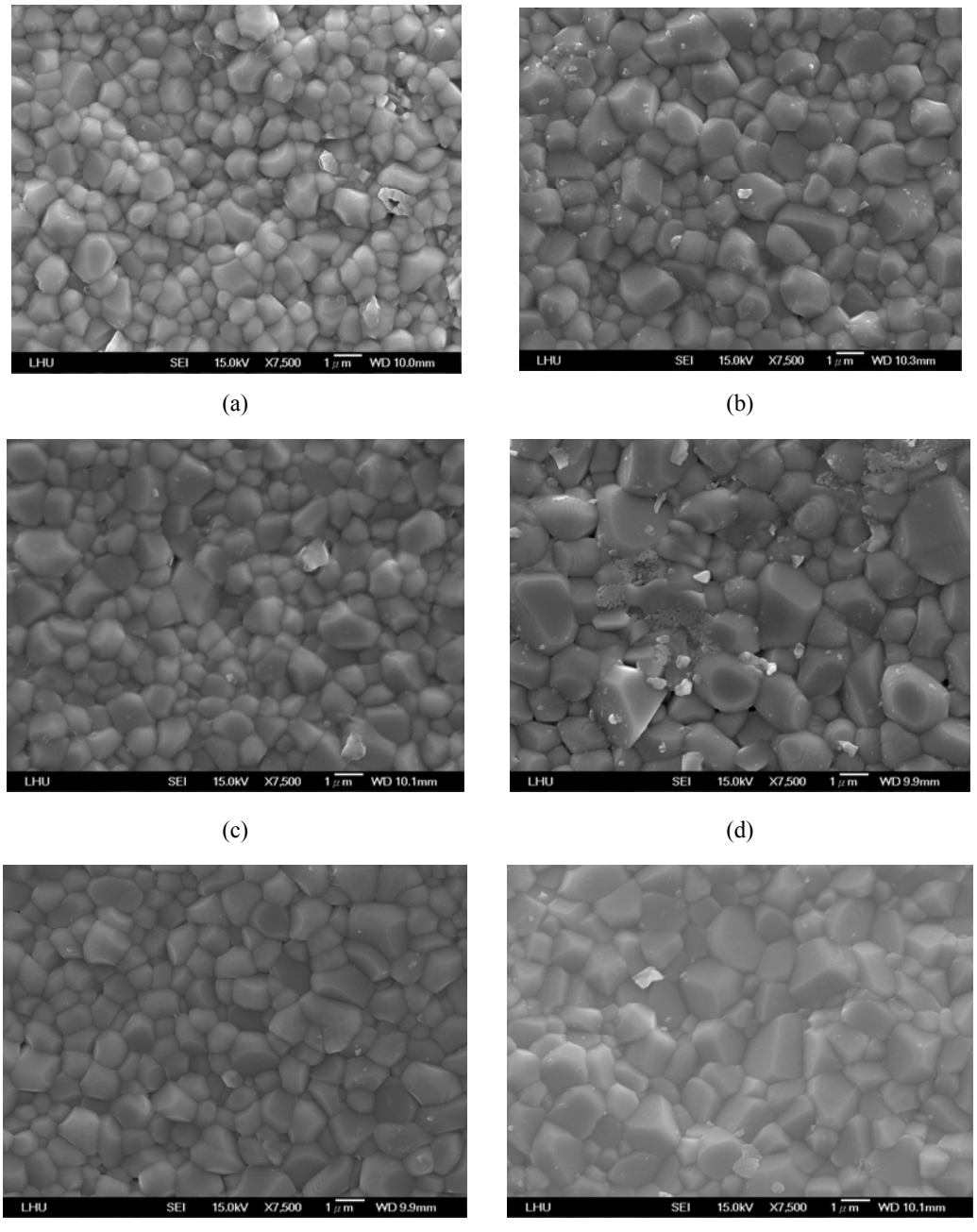

Fig. 3 Microstructures of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics sintered under different temperatures for 4 h: (a) x=0.025/1450 ^{O}C, (b) x=0.025/1500 ^{O}C, (c) x=0.025/1550 ^{O}C, (d) x=0.025/1600 ^{O}C, (e) x=0.05/1550 ^{O}C, (f) x=0.1/1550 ^{O}C.

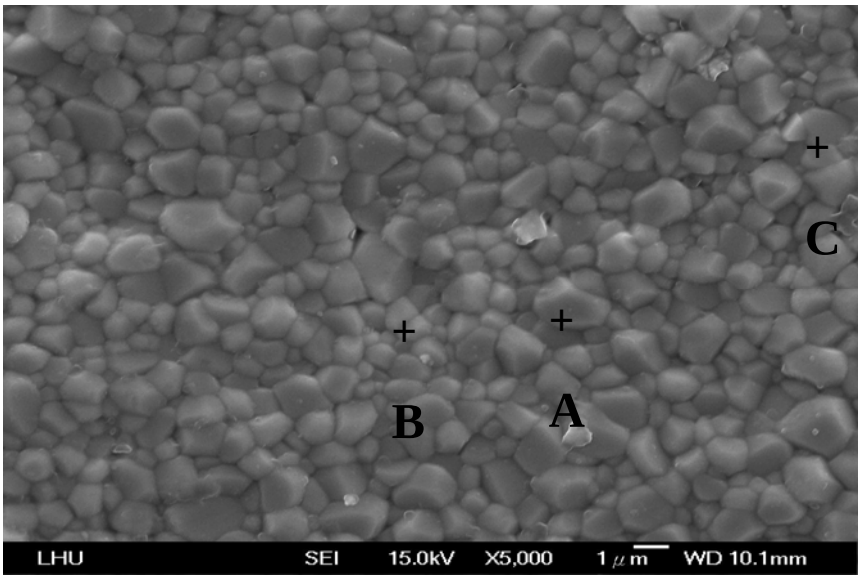

Fig. 4 Energy-dispersion spectroscopy (EDS) analysis of grains of $La(Mg_{0.5}Sn_{0.475}Ti_{0.025})O_3$ ceramics sintered at 1550 °C for 4 h.

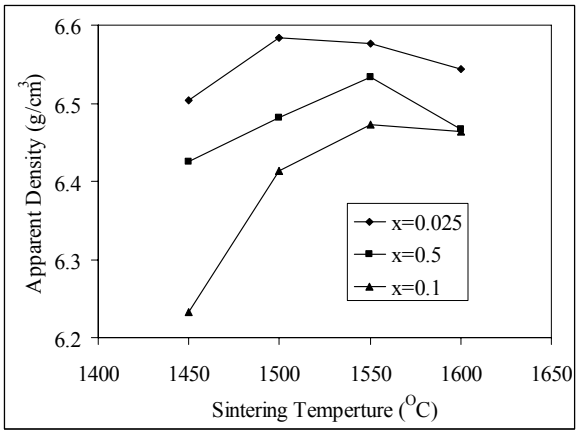

Fig. 5 Apparent densities of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics with different degrees of Ti^{4+} substitution, following sintering at different temperatures for 4 h.

Table 1. EDS data of grains of $La(Mg_{0.5}Sn_{0.475}Ti_{0.025})O_3$ ceramics sintered at 1550 °C for 4 h.

Atomic element	La (%)	Mg (%)	Sn (%)	Ti (%)	O (%)
A	15.55	6.92	7.74	0.46	69.33
B	18.97	9.74	8.09	0.51	62.69
C	15.35	0	12.31	0	72.34

Fig. 5 shows the apparent densities of the $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics with different degrees of Ti^{4+} substitution, following sintering at 1450-1600 °C for 4 h. The apparent density of the $La(Mg_{0.5}Sn_{0.475}Ti_{0.025})O_3$ ceramics that were sintered at 1450-1600 °C for 4 h was highest when sintering was carried out at 1500 °C, beyond which temperature, it decreased. The increase in apparent density may be caused by the decrease in the number of pores and a decrease in apparent density may be caused by the abnormal grain growth, as shown in Fig. 3. The densification temperature increased as the degree of Ti^{4+} substitution increased. The maximum apparent density decreased from 6.58 to 6.47 g/cm^3 as x increased from 0.025 to 0.1. The decrease in apparent density is associated with the fact that the Ti atom has a lower mass than the Sn atom.

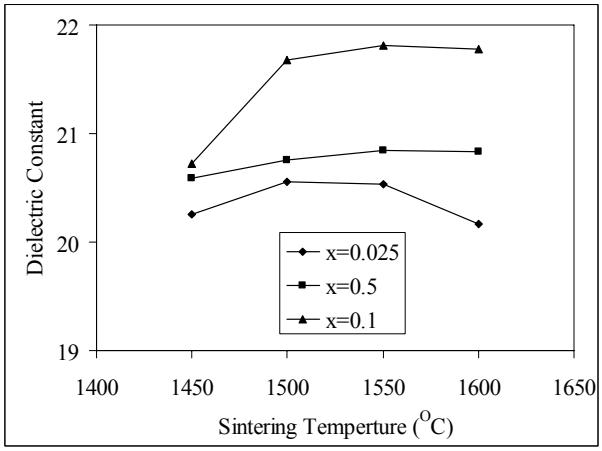

Fig. 6 Dielectric constants of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics with different degrees of Ti^{4+} substitution, following sintering at different temperatures for 4h.

Fig. 6 shows the dielectric constants of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics with different degrees of Ti^{4+} substitution, following sintering at 1450-1600 ^{O}C for 4 h. $La(Mg_{0.5}Sn_{0.4}Ti_{0.1})O_3$ ceramics that were sintered at 1550 ^{O}C for 4 h had a maximum dielectric constant of 21.8. A high sintering temperature was not necessary for obtaining a high dielectric constant. The decrease in dielectric constant was associated with low densities of the ceramics. A higher density is associated with lower porosity, and, therefore, a higher dielectric constant. The dielectric constant increased from 20.5 to 21.8 as the x increased from 0.025 to 0.1 when the $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics were sintered at 1550 ^{O}C for 4 h. Table II shows the dielectric constant of $La(Mg_{0.5}Sn_{0.5})O_3$ and $La(Mg_{0.5}Sn_{0.45}Ti_{0.05})O_3$ ceramics with different degrees of Ti^{4+} substitution sintered at 1500 ^{O}C for 4 h. The dielectric constant of $La(Mg_{0.5}Sn_{0.5})O_3$ and $La(Mg_{0.5}Sn_{0.45}Ti_{0.05})O_3$ ceramics sintered at 1500 ^{o}C for 4 h was 15.6 and 20.7, respectively. These results suggest that the dielectric constant was effectively increased by substituting some of the Sn^{4+} ions with Ti^{4+} ions. This fact might be explained by the volume of cation sites, as suggested by Tohto *et al* [13]. The dielectric constant can be calculated by Clausius-Mossotti equation:

$$\varepsilon_r = \frac{3V_{\mathrm{m}} + 8\pi\alpha_D}{3V_{\mathrm{m}} - 4\pi\alpha_D} \tag{2}$$

where Vm is the molar volume, α_D is the sum of ionic polarizabilities of individual ions. The Ti^{4+} ions with smaller ionic radius occupy Sn^{4+} ions, and with smaller molar volume, and, therefore, a higher dielectric constant. Dielectric constants are dependent on the ionic polarization. Larger the ionic polarization, higher will be the dielectric constant. The polarization of Ti^{4+} ion and Sn^{4+} ion are 2.93 and 2.83 $\AA^3$, respectively [14-15]. The dielectric constant of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics increased as x increased.

Table 2. Comparison the microwave dielectric properties of $La(Mg_{0.5}Sn_{0.5})O_3$ and $La(Mg_{0.5}Sn_{0.45}Ti_{0.05})O_3$ sintered at 1500 ^{O}C for 4 h.

Material	ε_r	Q×f (GHz)
$La(Mg_{0.5}Sn_{0.5})O_3$[6]	15.6	30,600
$La(Mg_{0.5}Sn_{0.45}Ti_{0.05})O_3$	20.7	43,400

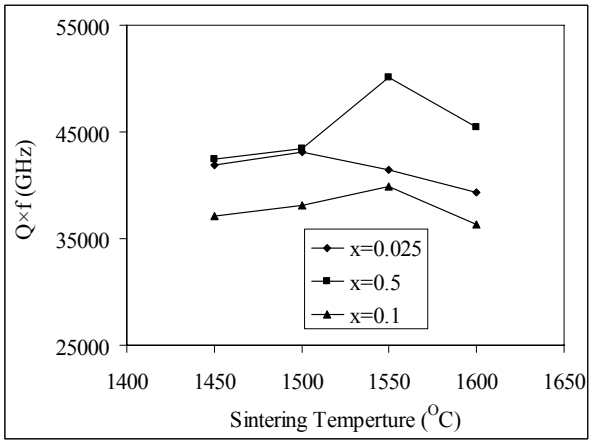

Fig. 7 $Q \times f$ of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics with different degrees of Ti^{4+} substitution, following sintering at different temperatures for 4h.

Fig. 7 shows the Q×f of the $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics with different degrees of Ti^{4+} substitution, following sintering at 1450-1600 ^{O}C for 4h. The Q×f of the $La(Mg_{0.5}Sn_{0.45}Ti_{0.05})O_3$ ceramics increased from 42,500 to 50,100 GHz as the temperature of sintering for 4 h increased from 1450 to 1550 ^{O}C. The relationship between the Q×f and the sintering temperature was consistent with that between the apparent density and the sintering temperature, because the microwave dielectric loss is affected by many factors, which is composed of intrinsic and extrinsic losses. Intrinsic loss is associated with the vibrational modes of the lattice. Extrinsic loss is associated with the density, porosity, second phases, impurities, oxygen vacancies, grain size, and lattice defects [16-17]. Since the Q×f was consistent with the variation of the apparent density, it is suggested to be dominated by the apparent density. The highest Q×f of 50,100 GHz was obtained for $La(Mg_{0.5}Sn_{0.45}Ti_{0.05})O_3$ ceramics that were sintered at 1550 ^{O}C for 4 h. Since the $La_2Sn_2O_7$ intensity of the second phase of the $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics was lowest when x was 0.05. Second phase of $La_2Sn_2O_7$ of the $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics is inferred to decrease the Q×f. Table II shows the Q×f of $La(Mg_{0.5}Sn_{0.5})O_3$ and $La(Mg_{0.5}Sn_{0.45}Ti_{0.05})O_3$ ceramics sintered at 1500 ^{O}C for 4 h are 30,600 and 43,400 GHz, respectively. These results suggest that the Q×f increased by partially substituting Sn^{4+} ions with Ti^{4+} ions.

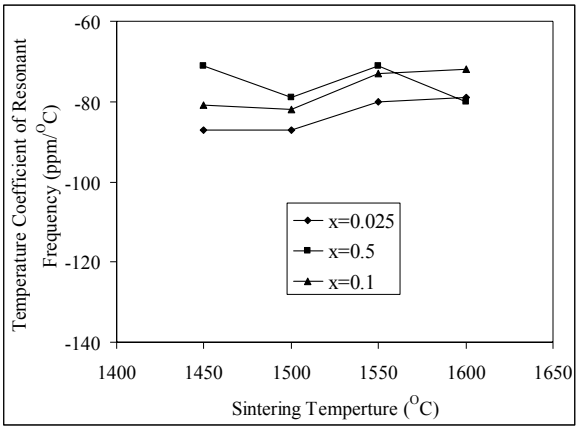

Fig. 8 τ_f of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics with different degrees of Ti^{4+} substitution, following sintering at different temperatures for 4h.

Fig. 8 shows the temperature coefficient of resonant frequency (τ_f) of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics with different degrees of Ti^{4+} substitution, following sintering at 1450-1600 ^{O}C for 4h. Generally, τ_f is related to the composition, the amounts of additive, and the second phases that are presented in the ceramics. No significant variation in τ_f of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics with sintering temperature over the entire range of sintering temperatures considered herein was observed. Since the composition of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics with a fixed amount of Ti^{4+} substitution did not vary with sintering temperature. The τ_f of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics were measured as a function of the amounts of Ti^{4+} substitution in this experiment. As the x increased from 0.025 to 0.05, the average value of τ_f increased from -83 to -75 ppm/^{O}C for the $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics sintered from 1450 to 1600 ^{O}C. The increase in τ_f was associated with tolerance factor of the ceramics. Sine the tolerance factor of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics increased as x increased. The τ_f became less negative as the tolerance factor increased [18,19]. As x increased from 0.05 to 0.1, the average value of τ_f decreased from -75 to -77 ppm/^{O}C for the $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics sintered from 1450 to 1600 ^{O}C. This is associated with the second phase. The $La_2Sn_2O_7$ intensity of the second phase of the $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics increased as x increased from 0.05 to 0.1. $La_2Sn_2O_7$ is inferred to have more negative τ_f compared to $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramic. A τ_f of -71 ppm/^{O}C was measured for $La(Mg_{0.5}Sn_{0.45}Ti_{0.05})O_3$ ceramics that were sintered at 1550 ^{O}C for 4 h.

4. Conclusions

The effects of the degree of Ti^{4+} substitution and sintering temperature on the microwave dielectric properties of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics were studied. The microwave dielectric properties of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics were improved by substituting Sn^{4+} ions with Ti^{4+} ions. The X-ray diffraction peaks of $La(Mg_{0.5}Sn_{0.45}Ti_{0.05})O_3$ ceramic did not vary significantly with sintering temperatures. The intensity of $La_2Sn_2O_7$ was lowest when x was 0.05. $La(Mg_{0.5}Sn_{0.45}Ti_{0.05})O_3$ ceramics that were sintered at 1550 ^{O}C for 4 h had an apparent density of 6.53 g/cm^3, a dielectric constant of 20.8, a Q×f of 50,100 GHz, and a temperature coefficient of resonant frequency (τ_f) of -71 ppm/^{O}C. The dielectric constant of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics is significantly affected by the degree of Ti^{4+} substitution. The Q×f of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics depend strongly on the apparent density and the second phase. The τ_f of $La(Mg_{0.5}Sn_{0.5-x}Ti_x)O_3$ ceramics is affected by the degree of Ti^{4+} substitution and the second phase.

Acknowledgments

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