Enhancement microwave dielectric properties of La($Mg_{0.5}Sn_{0.5}$)O_3 ceramics by substituting Mg^{2+} with Ni^{2+}

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ABSTRACT

The microwave dielectric properties of La($Mg_{0.5-x}Ni_xSn_{0.5}$)O_3 ceramics were examined with a view to their exploitation for mobile communication. The La($Mg_{0.5-x}Ni_xSn_{0.5}$)O_3 ceramics were prepared by the conventional solid-state method at various sintering temperatures. The X-ray diffraction patterns of the La($Mg_{0.4}Ni_{0.1}Sn_{0.5}$)O_3 ceramics revealed no significant variation of phase with sintering temperatures. Apparent density of 6.71 g/cm³, dielectric constant (ε_r) of 20.19, quality factor ($Q \times f$) of 74,600 GHz, and temperature coefficient of resonant frequency (τ_f) of −85 ppm/°C were obtained for La($Mg_{0.4}Ni_{0.1}Sn_{0.5}$)O_3 ceramics that were sintered at 1550 °C for 4 h.

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1. Introduction

The advantages provided by 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. A dielectric constant of 19.3 and a $Q \times f$ of 43,300 GHz were obtained when Nd($Mg_{0.5}Sn_{0.5}$)O_3 ceramics were sintered at 1550 °C for 4 h [1]. 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 °C for 4 h [2]. A liquid phase flux such as CuO and B_2O_3 was added to improve the microwave dielectric properties 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 that were sintered at 1550 °C for 4 h [3]. 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 and a $Q \times f$ of 45,000 GHz [4]. La$_{2.98/3}$Ba$_{0.01}$($Mg_{0.5}Sn_{0.5}$)O_3 have been synthesized with La^{3+} ions substituted partially with Ba^{2+} ions to improve the microwave dielectric properties. A dielectric constant of 19.8, and a $Q \times f$ of 46,500 GHz were obtained for La$_{2.98/3}$Ba$_{0.01}$($Mg_{0.5}Sn_{0.5}$)O_3 ceramics with 0.25 wt% B_2O_3 additive sintered at 1400 °C for 4 h [5]. Since the ionic radius of Bi^{3+} (0.103 nm) is similar to that of La^{3+} (0.1032 nm), the La^{3+} ion can be substituted by the Bi^{3+} ion to form La$_{1-x}$Bi$_x$($Mg_{0.5}Sn_{0.5}$)O_3 ceramics. A dielectric constant of 20.2 and a $Q \times f$ of 58,100 GHz were obtained for La$_{0.97}$Bi$_{0.03}$($Mg_{0.5}Sn_{0.5}$)O_3 ceramics that were sintered at 1550 °C for 4 h [6]. Combining two compounds with negative and positive temperature coefficients of resonant frequency is effective approach to obtain a near zero temperature coefficient of resonant frequency. 0.4La($Mg_{1/2}Ti_{1/2}$)O_3–0.6($Na_{0.5}Nd_{0.5}$)TiO_3 ceramics with 1 wt% B_2O_3 addition possesses a dielectric constant of 42, a $Q \times f$ of 33,000 GHz and a temperature coefficient of resonant frequency of 0.5 ppm/°C that were sintered at 1475 °C [7]. 0.55La($Mg_{1/2}Ti_{1/2}$)O_3–0.45SrTiO$_3$ ceramics with 0.25% B_2O_3 sintered at 1475 °C for 4 h in air exhibited optimum microwave dielectric properties of dielectric constant of 46.32, a $Q \times f$ of 34,000 GHz and a temperature coefficient of resonant frequency of −0.12 ppm/°C [8]. At 1425 °C, 0.87La($Mg_{1/2}Ti_{1/2}$)O_3–0.13Ca$_{0.8}$Sr$_{0.2}$TiO$_3$ ceramics with 0.5 wt% B_2O_3 addition possesses a dielectric constant of 38.3, a $Q \times f$ value of 59,800 GHz and a temperature coefficients of resonant frequency of 0 ppm/°C [9]. 0.4La($Mg_{1/2}Ti_{1/2}$)O_3–0.6($Na_{0.5}Nd_{0.5}$)TiO_3 ceramics with 1 wt% B_2O_3 addition possesses a dielectric constant of 42, a $Q \times f$ of 33,000 GHz and a temperature coefficient of resonant frequency of 0.5 ppm/°C that were sintered at 1475 °C [7]. At 1475 °C, 0.6La($Mg_{1/2}Ti_{1/2}$)O_3–0.4Ca$_{0.6}$Nd$_{0.8/3}$TiO$_3$ ceramics with 0.5 wt% B_2O_3 addition possesses a dielectric constant of 39, a $Q \times f$ of 41,000 GHz and a temperature coefficient of resonant frequency of −2.6 ppm/°C [10]. The optimum combination of microwave dielectric properties was achieved at 1475 °C for samples where 0.5La($Mg_{0.5}Ti_{0.5}$)O_3–0.5(Ca$_{0.8}$Sr$_{0.2}$)TiO$_3$

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with a dielectric constant of 47.12, a $Q \times f$ value of 35,000 GHz and a temperature coefficient of resonant frequency value of -4.7 ppm/°C [11]. A new microwave dielectric material $0.45La(Mg_{0.5}Ti_{0.5})O_3–0.55Ca_{0.8}Sm_{0.4/3}TiO_3$, possessing a fine combination of microwave dielectric properties with a dielectric constant of 47.83, a $Q \times f$ of 26,500 GHz and a temperature coefficient of resonant frequency of -1.7 ppm/°C [12]. $0.6La(Mg_{1/2}Ti_{1/2})O_3–0.4(La_{0.5}Na_{0.5})TiO_3$ ceramics with 1 wt% B_2O_3 addition possesses a dielectric constant of 36, a $Q \times f$ value of 25,500 GHz and a temperature coefficients of resonant frequency of -5 ppm/°C sintering at 1475 °C [13]. A dielectric constant of 37, a $Q \times f$ value of 34,100 GHz and a temperature coefficient of resonant of 13.5 ppm/°C were obtained for $0.1CaTiO_3–0.9Nd(Mg_{1/2}Ti_{1/2})O_3$ ceramics that sintered at 1325 °C for 4 h [14]. At 1375 °C, $0.4Nd(Mg_{1/2}Ti_{1/2})O_3–0.6Ca_{0.6}La_{0.8/3}TiO_3$ ceramics with 1 wt% B_2O_3 addition possesses a dielectric constant of 49, a $Q \times f$ value of 13,000 GHz and a temperature coefficients of resonant frequency of 1 ppm/°C [15]. At 1475 °C, $0.1SrTiO_3–0.9Nd(Mg_{1/2}Ti_{1/2})O_3$ has a dielectric constant of 45.4, a $Q \times f$ value of 44,000 GHz and a temperature coefficient of resonant frequency of -3 ppm/°C [16].

Since the ionic radius of Ni^{2+} (0.069 nm) is similar to that of Mg^{2+} (0.072 nm), the Mg^{2+} ion can be replaced by with the Ni^{2+} ion to form $La(Mg_{0.5-x}Ni_xSn_{0.5})O_3$ [17]. In this investigation, $La(Mg_{0.5-x}Ni_xSn_{0.5})O_3$ were synthesized and some of the Mg^{2+} ions were substituted with Ni^{2+} ions to improve their microwave dielectric properties. Moreover, the effect of the sintering temperature on the microwave dielectric properties of $La(Mg_{0.5-x}Ni_xSn_{0.5})O_3$ ceramics was studied. $La(Mg_{0.5-x}Ni_xSn_{0.5})O_3$ ceramics were synthesized 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 $La(Mg_{0.5-x}Ni_xSn_{0.5})O_3$ ceramics were found to vary with the degree of Ni^{2+} 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 La_2O_3 (99.99%), MgO (98.0%), NiO (99.97%), and SnO_2 (99.0%) powder. The prepared composition was $La(Mg_{0.5-x}Ni_xSn_{0.5})O_3$. Specimens were prepared using the conventional mixed-oxide method. The raw material was weighed out in stoichiometric proportions 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 °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. This finer powder was then axially pressed at 2000 kg/cm² into pellets with a diameter of 11 mm and a thickness of 6 mm. The specimens thus obtained were then sintered at temperatures of 1450–1600 °C for 4 h in air. Both the heating rate and the cooling rate were set to 10 °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 CuKα radiation (at 30 kV and 20 mA) and a graphite monochromator in the 2θ range of 20°–80°. Scanning electron microscopy (SEM; JEOL JSM-6500F) and energy dispersive X-ray spectrometer (EDS) were utilized to examine the microstructures of the specimens. The apparent densities of the specimens were measured by 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 [18]. This method employs 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 that was determined by Kobayashi and Katoh [19]. 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 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 °C. The τ_f value (ppm/°C) was determined from the change in resonant frequency: (1) $\tau_f = \frac{f_2-f_1}{f_1(T_2-T_1)}$ 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 $La(Mg_{0.4}Ni_{0.1}Sn_{0.5})O_3$ ceramics that were sintered at 1450–1600 °C for 4 h. Clearly, $La(Mg_{0.4}Ni_{0.1}Sn_{0.5})O_3$ is the main crystalline phase, which is accompanied by small amounts of $La_2Sn_2O_7$ as the second phase. The formation of $La_2Sn_2O_7$ might deteriorate the dielectric constant and quality factor of the specimen. A later investigation will involve preparation of the powder by precipitation from solution. Such a method may yield a single-phase product. A single-phase product potentially has much higher values of the parameters of interest. 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. According to Glazer, the superlattice reflections, with specific combinations of odd (o) and even (e) Miller indices, reveal particular deviations of the structure from the undistorted cubic structure, such as octahedral in-phase tilting (o o e, o e o, e o o), anti-phase tilting (o o o, $h + k + l > 3$), and anti-parallel displacement of A-cations (e e o, e o e, o e e) [20]. 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 1/2(4 4 1)) extra peaks indicate A-site cation displacement, the (1/2(3 1 1), 1/2(3 3 1), 1/2(5 1 1) and 1/2(5 3 1)) peaks reveal anti-phase tilting, and the 1/2(3 2 1) peak show in-phase tilting. The X-ray diffraction patterns of $La(Mg_{0.4}Ni_{0.1}Sn_{0.5})O_3$ ceramics did not significantly vary with sintering temperature. Fig. 2 shows the X-ray diffraction patterns of $La(Mg_{0.5-x}Ni_xSn_{0.5})O_3$ ceramics as x is varied from 0 to 0.15, following sintering at 1550 °C for 4 h. The diffraction peaks of $La(Mg_{0.5-x}Ni_xSn_{0.5})O_3$ ceramics shifted to higher angles as x increased, perhaps because the ionic
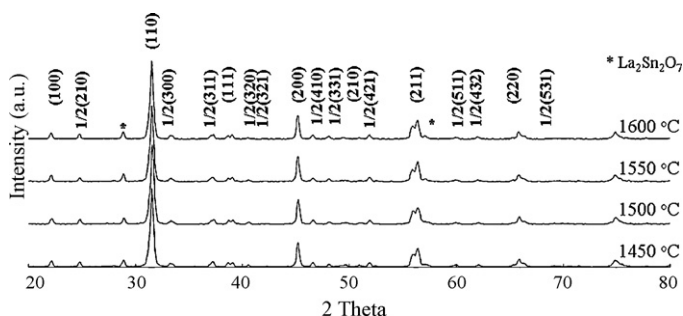

Fig. 1. X-ray diffraction patterns of $La(Mg_{0.4}Ni_{0.1}Sn_{0.5})O_3$ specimens sintered at 1450–1600 °C for 4 h (*: $La_2Sn_2O_7$).
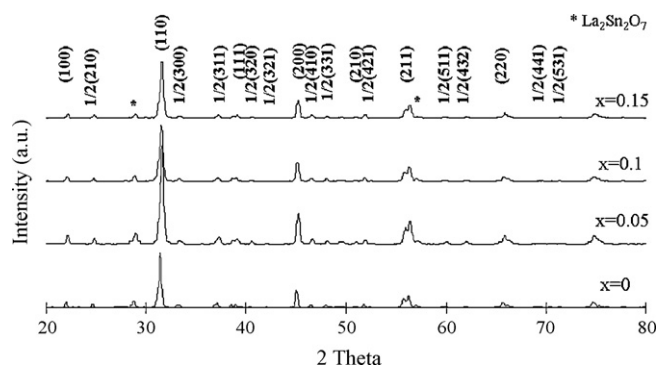
Fig. 2. X-ray diffraction patterns of $La(Mg_{0.5-x}Ni_xSn_{0.5})O_3$ ceramics that were sintered at 1550 °C for 4 h (*: $La_2Sn_2O_7$).

Table 1
Amount of main phase, grain size and $Q \times f$ of La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics following sintering at 1550 °C for 4 h.

Material	Main phase (%)	Grain size (μm)	$Q \times f$ (GHz)
La(Mg$_{0.5}$Sn$_{0.5}$)O$_3$	89.09	0.85	45,900
La(Mg$_{0.45}$Ni$_{0.05}$Sn$_{0.5}$)O$_3$	89.77	1.49	64,400
La(Mg$_{0.4}$Ni$_{0.1}$Sn$_{0.5}$)O$_3$	90.14	1.43	74,600
La(Mg$_{0.35}$Ni$_{0.15}$Sn$_{0.5}$)O$_3$	91.98	1.29	39,000

Table 2
EDS data of grains of La(Mg$_{0.4}$Ni$_{0.1}$Sn$_{0.5}$)O$_3$ ceramics sintered at 1550 °C for 4 h.

Atomic element	La (%)	Mg (%)	Ni (%)	Sn (%)	O (%)
A	17.48	0.00	0.00	16.33	66.19
B	17.05	7.48	0.86	8.27	66.35
C	14.27	6.54	1.28	6.85	71.05

radius of Ni^{2+} ions (0.069 nm) is smaller than that of Mg^{2+} ions (0.072 nm). The amount of main phase was evaluated from most intensive lines of main and second phases,

$$\text{Main phase} \ (\%) = \frac{I_{\text{main}}}{I_{\text{main}} + I_{\text{second}}} \times 100, \tag{2}$$

where I_{main} is the most intensive line of main phase and I_{second} is the most intensive line of second phase. Table 1 shows the amount of main phase of La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics that were sintered at 1550 °C for 4 h. The amount of main phase increased from 89.09% to 91.98% as x increased from 0 to 0.15. The tolerance factors of La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics increased from 0.914 to 0.916 as x increased from 0 to 0.15. The tolerance factors were calculated using the ionic radius data of Shannon [17]. The tolerance factors of La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ series are in the anti-phase and in-phase titled region [21], which is in agreement with those of X-ray diffraction patterns as describe above.

Fig. 3 shows the microstructures of La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics following sintering for 4 h at different temperatures. The microstructures of La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics when Mg^{2+} ions were replaced with different degrees of Ni^{2+} ions indicated that the average grain size did not vary significantly with x varied from 0.05 to 0.10. The average grain size decreased from 1.43 to 1.29 μm as x increased from 0.1 to 0.15. Comparing the microstructures of La(Mg$_{0.4}$Ni$_{0.1}$Sn$_{0.5}$)O$_3$ ceramics that were sintered under different temperatures indicated that the average grain size increased from 1.16 to 1.64 μm as sintering temperature increased from 1450 to 1600 °C. The pores of La(Mg$_{0.4}$Ni$_{0.1}$Sn$_{0.5}$)O$_3$ ceramics almost disappeared upon sintering at 1550 °C for 4 h. To identify the composition of the second phase, energy-disperse spectroscopy (EDS) analysis was carried out on the grains of La(Mg$_{0.4}$Ni$_{0.1}$Sn$_{0.5}$)O$_3$ ceramics that were sintered at 1550 °C for 4 h, as shown in Fig. 3(d). According to the quantitative analysis, as shown in Table 2, the A grain is La$_2$Sn$_2$O$_7$ and the B and C grains are La(Mg$_{0.4}$Ni$_{0.1}$Sn$_{0.5}$)O$_3$.
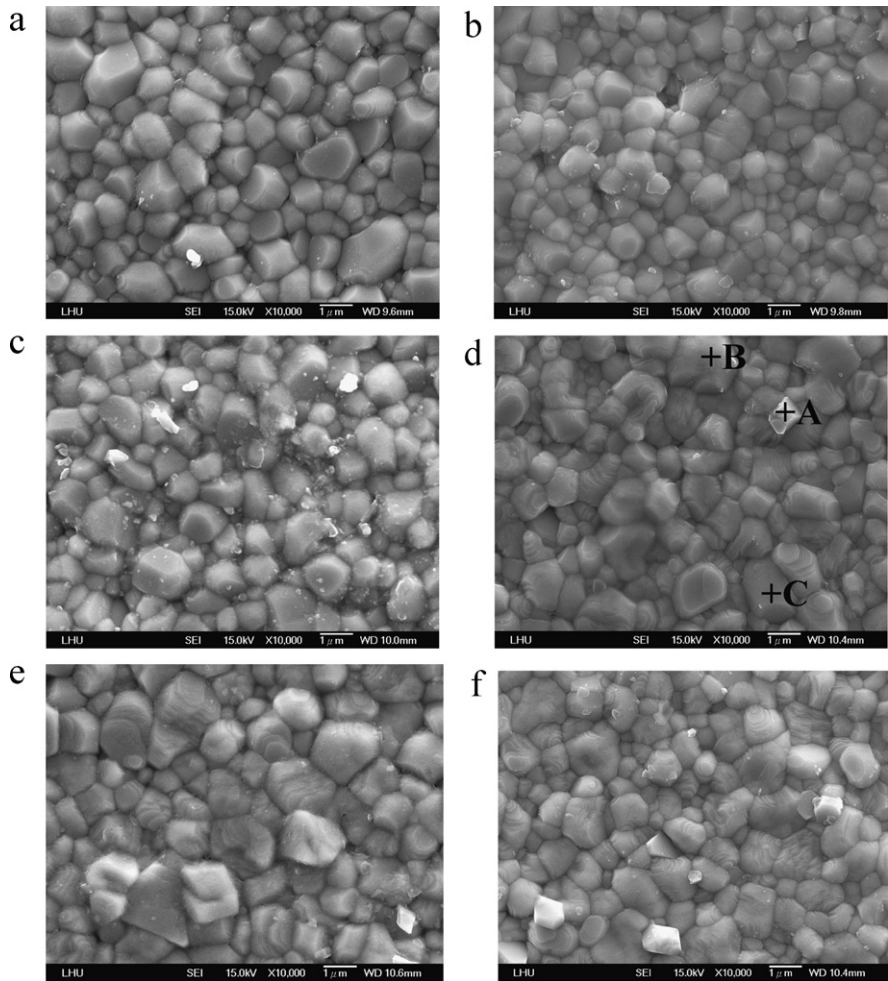
Fig. 3. Microstructures of La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics sintered under different temperatures for 4 h: (a) $x = 0.05/1550$ °C, (b) $x = 0.1/1450$ °C, (c) $x = 0.1/1500$ °C, (d) $x = 0.1/1550$ °C, (e) $x = 0.1/1600$ °C, and (f) $x = 0.15/1550$ °C.
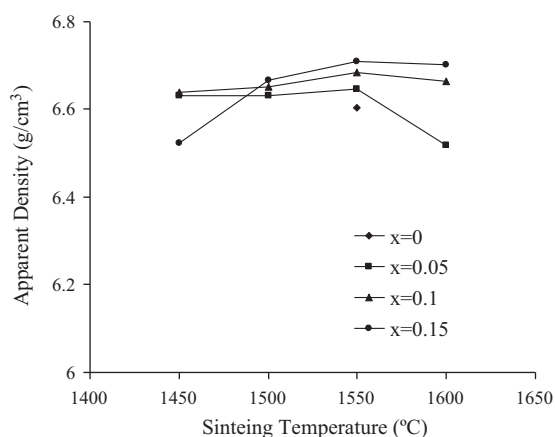
Fig. 4. Apparent densities of La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics with different degrees of Ni^{2+} substitution, following sintering at different temperatures for 4 h.

Fig. 6. $Q \times f$ of La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics with different degrees of Ni^{2+} substitution, following sintering at different temperatures for 4 h.

Fig. 4 shows the apparent densities of La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics with different degrees of Ni^{2+} substitution, following sintering at 1450–1600 °C for 4 h. The theoretical density of La(Mg$_{0.5}$Sn$_{0.5}$)O$_3$ ceramic is 6.63 g/cm^3. The apparent density of La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics that were sintered at 1450–1600 °C for 4 h was highest when sintering was carried out at 1550 °C, beyond which temperature, it decreased. The increase in apparent density may be caused by the decrease in the number of pores, as shown in Fig. 3. The maximum apparent density of La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics increased from 6.60 to 6.71 g/cm^3 as x increased from 0 to 0.15. The increase in apparent density is associated with the fact that the Ni atom has a larger mass than the Mg atom.

Fig. 5 shows the dielectric constants of La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics with different degrees of Ni^{2+} substitution, following sintering at 1450–1600 °C for 4 h. La(Mg$_{0.35}$Ni$_{0.15}$Sn$_{0.5}$)O$_3$ ceramics that were sintered at 1550 °C for 4 h had a maximum dielectric constant of 20.24. A high sintering temperature was not necessary for obtaining a high dielectric constant. The decrease in dielectric constant was associated with low apparent densities of the ceramics. A higher density is associated with lower porosity, and, therefore, a higher dielectric constant. The dielectric constant increased from 19.94 to 20.24 as x increased from 0 to 0.15 when the La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics were sintered at 1550 °C for 4 h. This fact might be explained by the molar volume. The dielectric
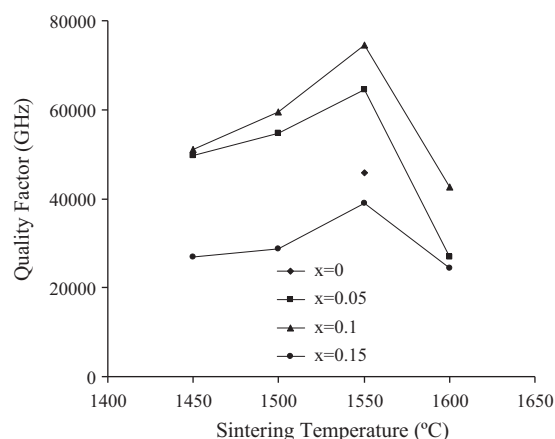
constant can be calculated using the Clausius–Mossotti equation [22]:

$$\varepsilon_r = \frac{3V_m + 8\pi\alpha_D}{3V_m - 4\pi\alpha_D} = \frac{1 + (8\pi/3)(\alpha_D/V_m)}{1 - (4\pi/3)(\alpha_D/V_m)} \tag{3}$$

where V_m is the molar volume, α_D is the sum of the ionic polarizations of individual ions. Dielectric constants therefore depend on the ionic polarization and the molar volume. As seen from Eq. (3), a larger ionic polarization or a smaller molar volume, is associated with a larger obtained dielectric constant. The polarizations of Mg^{2+} ion and Ni^{2+} ion are 1.32 and 1.23 Å^3, respectively [23,24]. The polarization of Mg^{2+} ion is almost the same as that of Ni^{2+} ion. However, the Ni^{2+} ions with smaller ionic radius occupy Mg^{2+} ions, and with smaller molar volume, and, therefore, a higher dielectric constant.

Fig. 6 shows the $Q \times f$ of the La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics with different degrees of Ni^{2+} substitution, following sintering at 1450–1600 °C for 4 h. La(Mg$_{0.4}$Ni$_{0.1}$Sn$_{0.5}$)O$_3$ ceramics that were sintered at 1550 °C for 4 h had the highest $Q \times f$ of 74,600 GHz. The microwave dielectric loss is affected by many factors, which is composed of intrinsic and extrinsic losses. Intrinsic loss is associated with the vibration modes of the lattice. Extrinsic loss is associated with the density, porosity, second phases, impurities, oxygen vacancies, grain size, and lattice defects [25,26]. Since the $Q \times f$ of La(Mg$_{0.4}$Ni$_{0.1}$Sn$_{0.5}$)O$_3$ ceramics was consistent with the variation of the apparent density, it is suggested to be dominated by the apparent density. When the La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics were sintered at 1550 °C for 4 h, the $Q \times f$ increased from 45,900 to 74,600 GHz as x increased from 0 to 0.1, then decreased from 74,600 to 39,000 GHz as x increased from 0.1 to 0.15. The increase in $Q \times f$ as x increased from 0 to 0.1 and decrease in $Q \times f$ as x increased from 0.1 to 0.15 might be explained from grain size. Table 1 shows the grain sizes of La(Mg$_{0.5}$Sn$_{0.5}$)O$_3$, La(Mg$_{0.4}$Ni$_{0.1}$Sn$_{0.5}$)O$_3$, and La(Mg$_{0.35}$Ni$_{0.15}$Sn$_{0.5}$)O$_3$ are 0.85, 1.43 and 1.29 μm, respectively. The total number of the grain boundaries decreased as the average grain size increased. Gran boundaries acted as plane defects [27]. Less grain boundaries in La(Mg$_{0.4}$Ni$_{0.1}$Sn$_{0.5}$)O$_3$ ceramics compared with that of La(Mg$_{0.5}$Sn$_{0.5}$)O$_3$ and La(Mg$_{0.35}$Ni$_{0.15}$Sn$_{0.5}$)O$_3$. Besides density and grain size, the amount of second phase also plays an important role in affecting $Q \times f$. The formation of second phase of La$_2$Sn$_2$O$_7$ might deteriorate the quality factor of the specimen. Table 1 shows the amount of main phase increased from 89.09% to 91.98% as x increased form 0 to 0.15, and, therefore, the amount of second phase La$_2$Sn$_2$O$_7$ decreased from 10.91% to 8.02%.
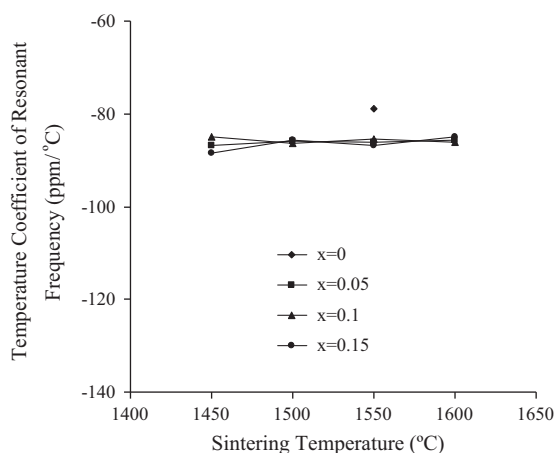

Fig. 5. Dielectric constants of La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics with different degrees of Ni^{2+} substitution, following sintering at different temperatures for 4 h.

Fig. 7. τ_f of La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics with different degrees of Ni^{2+} substitution, following sintering at different temperatures for 4 h.

Fig. 7 shows the temperature coefficient of resonant frequency (τ_f) of La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics with different degrees of Ni^{2+} substitution, following sintering at 1450–1600 °C for 4 h. Generally, τ_f is related to the composition, the amount of additive and the second phases that are present in the ceramics. No significant variation in τ_f of La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics with sintering temperature over the entire range of sintering temperatures considered herein was observed. Since the composition of La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics with a fixed amount of Ni^{2+} substitution did not vary with sintering temperature. Although the influence of the degrees of Ni^{2+} substitution on the dielectric constant and $Q \times f$ was observed as described above, no significant variation in τ_f was observed. For perovskite ceramic, the τ_f is related to the tilting of oxygen octahedron [21]. The tilting of oxygen octahedron is controlled by the tolerance factor of the perovskite ceramic. Since the variation of tolerance factor in La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ series was slight, the effect of tolerance factor on the τ_f can be ignored in this study. A τ_f of −85 ppm/°C was measured for La(Mg$_{0.4}$Ni$_{0.1}$Sn$_{0.5}$)O$_3$ ceramics that were sintered at 1550 °C for 4 h.

4. Conclusions

The effects of the degree of Ni^{2+} substitution and sintering temperature on the microwave dielectric properties of La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics were studied. The microwave dielectric properties of La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics were improved by substituting Mg^{2+} ions for Ni^{2+} ions. The X-ray diffraction peaks of La(Mg$_{0.4}$Ni$_{0.1}$Sn$_{0.5}$)O$_3$ ceramics did not vary significantly with sintering temperature. The diffraction peaks of La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics shifted to higher angles and the amount of second phase La$_2$Sn$_2$O$_7$ decreased as x increased. La(Mg$_{0.4}$Ni$_{0.1}$Sn$_{0.5}$)O$_3$ ceramics that were sintered at 1550 °C for 4 h had an apparent density of 6.71 g/cm^3, a dielectric constant of 20.19, a $Q \times f$ of 74,600 GHz, and a temperature coefficient of resonant frequency (τ_f) of −85 ppm/°C. The dielectric constant of La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics was affected by the density and ionic polarization. The $Q \times f$ of La(Mg$_{0.5-x}$Ni$_x$Sn$_{0.5}$)O$_3$ ceramics depended on the density, grain size, and amount of second phase.

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