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Crystal structure and dielectric properties of $La(Mg_{0.5}Ti_{0.5})O_3$–$Ca_{0.8}Sm_{0.4/3}TiO_3$ solid solution system at microwave frequencies

Jhih-Yong Chen, Cheng-Liang Huang*

Department of Electrical Engineering, National Cheng Kung University, Tainan 70101, Taiwan

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ABSTRACT

The crystal structure and the dielectric properties of $(1-x)La(Mg_{0.5}Ti_{0.5})O_3$–$xCa_{0.8}Sm_{0.4/3}TiO_3$ ceramics have been investigated. $Ca_{0.8}Sm_{0.4/3}TiO_3$ was employed as a τ_f compensator and was added to $La(Mg_{0.5}Ti_{0.5})O_3$ to achieve a temperature-stable material. The formation of $(1-x)La(Mg_{0.5}Ti_{0.5})O_3$–$xCa_{0.8}Sm_{0.4/3}TiO_3$ solid solutions were confirmed by the XRD results and the measured lattice parameters for all compositions. The dielectric properties are strongly correlated to the sintering temperature and the compositional ratio of the specimens. Although the ε_r of the specimen could be boosted by increasing the amount of $Ca_{0.8}Sm_{0.4/3}TiO_3$, it would instead render a decrease in the $Q\times f$. The τ_f value is strongly correlated to the compositions and can be controlled by the existing phases. 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 an ε_r of 47.83, a $Q\times f$ of 26,500 GHz (at 6.2 GHz) and a τ_f of −1.7 ppm/°C, is proposed as a very promising candidate material for today's 3G applications.

1. Introduction

Miniaturization of patch antennas for volume efficiency in global positioning system (GPS) has become a primary issue in these few years. In particular, materials with dielectric constant in the 40 s can reduce the antenna size from 25 mm × 25 mm to 18 mm × 18 mm or even to 15 mm × 15 mm. Several research efforts have recently been dedicated toward the development of such dielectric materials [1–4]. In addition, a high $Q\times f$ is also required [5,6] to simultaneously retain a small return loss and achieve a wide bandwidth of the GPS antennas for practical applications.

Several complex perovskites ceramics $A(B^{2+}_{1/2}B^{4+}_{1/2})O_3$ (where A = La, Nd, Sm; B^{2+} = Mg, Zn, Co, Ni, Mn; B^{4+} = Ti and Sn) have been reported due to their excellent microwave dielectric properties [1,7–11]. Among them, $La(Mg_{0.5}Ti_{0.5})O_3$ has a high dielectric constant ($\varepsilon_r\sim29$), a high quality factor ($Q\times f$ value ~75,500 GHz) and a negative τ_f value (−65 ppm/°C) [12,13]. In order to compensate the τ_f of the $La(Mg_{0.5}Ti_{0.5})O_3$, $CaTiO_3$ was added to form the $0.5La(Mg_{0.5}Ti_{0.5})O_3$–$0.5CaTiO_3$ solid solution with an $\varepsilon_r\sim43$–46.7, a $Q\times f$ value ~12,400–24,470 GHz and a τ_f value ~ −8.9 to −13 ppm/°C [14,15]. However, its $Q\times f$ still needs to be promoted before putting it to a practical application as GPS antennas. A number of dielectrics were also used as a τ_f compensator for $La(Mg_{0.5}Ti_{0.5})O_3$ [16–18].

$Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics ($\varepsilon_r\sim120$, $Q\times f\sim13{,}800$ GHz, $\tau_f\sim400$ ppm/°C) [19] having a much higher $Q\times f$ than that of $CaTiO_3$ was chosen as a τ_f compensator for $La(Mg_{0.5}Ti_{0.5})O_3$. Consequently, not only compensation for the τ_f can be made by employing the solid solutions of $0.45La(Mg_{0.5}Ti_{0.5})O_3$–$0.55Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics, it also shows a more than 13.7% promotion in the $Q\times f$ compared to that of $0.5La(Mg_{0.5}Ti_{0.5})O_3$–$0.5CaTiO_3$. In addition, the X-ray diffraction (XRD) patterning and scanning electron microscopy (SEM) analysis were also employed to study the crystal structures and microstructures of the ceramics. The correlation between the microstructure and the $Q\times f$ value was also investigated.

2. Experimental procedure

The starting materials were high-purity oxide powders (>99.9%): $CaCO_3$, Sm_2O_3, La_2O_3, MgO and TiO_2. The powders were separately prepared according to the desired stoichiometry $Ca_{0.8}Sm_{0.4/3}TiO_3$ and $La(Mg_{0.5}Ti_{0.5})O_3$, and ground in distilled water for 24 h in a ball mill with agate balls. The prepared powders were dried and calcined at 1200 °C for 4 h in air. After calcinations, the calcined powders were mixed according to the molar fraction $(1-x)La(Mg_{0.5}Ti_{0.5})O_3$–$xCa_{0.8}Sm_{0.4/3}TiO_3$ (x = 0.2–0.8) and then re-milled for 24 h. The fine powder with 3 wt% of a 10% solution of PVA as a binder (PVA 500, Showa, Japan) was pressed into pellets with dimensions of 11 mm in diameter and 5 mm in thickness under the pressure of 200 MPa. These pellets were sintered at temperatures of 1380–1530 °C for 4 h in air. The heating rate and the cooling rate were both set at 10 °C/min.

The bulk X-ray diffraction (XRD, Siemens D5000) spectra were collected using Cu Kα (λ = 0.15406 nm) radiation (at 40 kV and 40 mA) and a graphite monochrometer

* Corresponding author at: Department of Electrical Engineering, National Cheng Kung University, No. 1 University Road, Tainan 70101, Taiwan.
Tel.: +886 6 2757575x62390; fax: +886 6 2345482.
E-mail address: huangcl@mail.ncku.edu.tw (C.-L. Huang).

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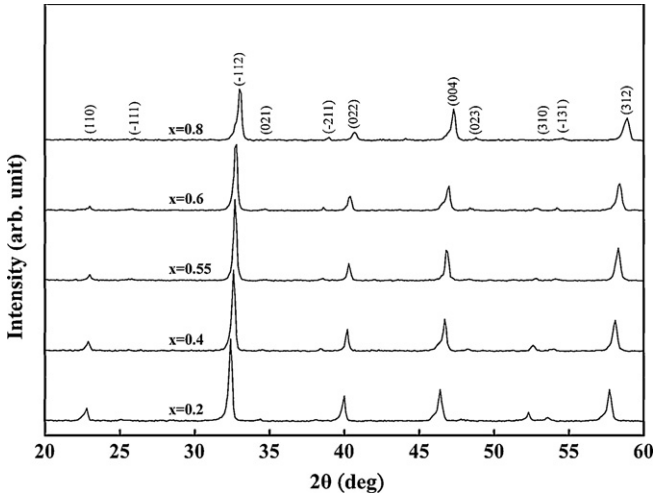

Fig. 1. X-ray diffraction patterns of $(1-x)La(Mg_{0.5}Ti_{0.5})O_3$–$xCa_{0.8}Sm_{0.4/3}TiO_3$ ceramic system sintered at 1470 °C for 4 h with different x values.

in the 2θ range of 20–60°. The microstructures were evaluated surfaces by scanning electron microscopy (SEM; Philips XL-40FEG, Eindhoven, The Netherlands). The apparent densities of the sintered pellets were measured by the Archimedes method. The dielectric constant (ε_r) and the quality factor values (Q) at microwave frequencies were measured using the Hakki–Coleman dielectric resonator method [20,21]. A system combining a HP8757D network analyzer and a HP8350B sweep oscillator was employed in the measurement. For temperature coefficient of resonant frequency (τ_f), the technique is the same as that of quality factor measurement. The test cavity is placed over a thermostat and the temperature range used is from +20 to +80 °C.

3. Results and discussion

Fig. 1 shows the XRD patterns of the $(1-x)La(Mg_{0.5}Ti_{0.5})O_3$–$xCa_{0.8}Sm_{0.4/3}TiO_3$ ceramic system sintered at 1470 °C for 4 h. As the x value increases, the peaks in the XRD spectra shift to a higher angle implying the forming of solid solution. This is because the ionic radii of Mg^{2+} (0.72 Å) in $La(Mg_{0.5}Ti_{0.5})O_3$ are larger than that of Ti^{4+} (0.605 Å) in $Ca_{0.8}Sm_{0.4/3}TiO_3$ [22]. From the study of Lee et al. [10], $La(Mg_{0.5}Ti_{0.5})O_3$ has the 1:1 ordered perovskite structure, which has an anti-parallel shift of the cation and the anti-phase and in-phase tilt of oxygen octahedral. Furthermore, the diffraction patterns showed that specimens using $(1-x)La(Mg_{0.5}Ti_{0.5})O_3$–$xCa_{0.8}Sm_{0.4/3}TiO_3$ with x = 0.2–0.8 possess a complex perovskite-structured (Monoclinic: ICDD-PDF #01-072-6152). The measured lattice parameters (Fig. 2) linearly varied from a = 5.5320 Å (±0.0021 Å), b = 5.5398 Å (±0.0023 Å), c = 7.8177 Å (±0.0027 Å) at x = 0.2 to a = 5.4473 Å (±0.0012 Å), b = 5.4507 Å (±0.0012 Å), c = 7.7064 Å (±0.0019 Å) at x = 0.8 further confirming it tends to form a continuous solid solution.

Table 1 demonstrates the microwave dielectric properties of $(1-x)La(Mg_{0.5}Ti_{0.5})O_3$–$xCa_{0.8}Sm_{0.4/3}TiO_3$ solid solution system sintered at 1470 °C for 4 h. As the x value increases from 0.2 to 0.8, the τ_f value of the specimen increases from −58.1 to 107.9 ppm/°C. It indicates that a zero τ_f value can be achieved by appropriately adjusting the x value of specimen because the τ_f curve goes through zero.

Table 1
Microwave dielectric properties of $(1-x)La(Mg_{0.5}Ti_{0.5})O_3$–$xCa_{0.8}Sm_{0.4/3}TiO_3$ ceramic system sintered at 1470 °C for 4 h.

x value	Apparent density (g/cm^3)	ε_r	$Q\times f$ (GHz)	τ_f (ppm/°C)
0.80	4.42	72.41	9700	107.9
0.60	4.76	50.58	20,300	13.7
0.55	4.86	47.83	26,500	−1.7
0.40	5.09	40.05	39,000	−38.9
0.20	5.44	33.56	52,700	−58.1

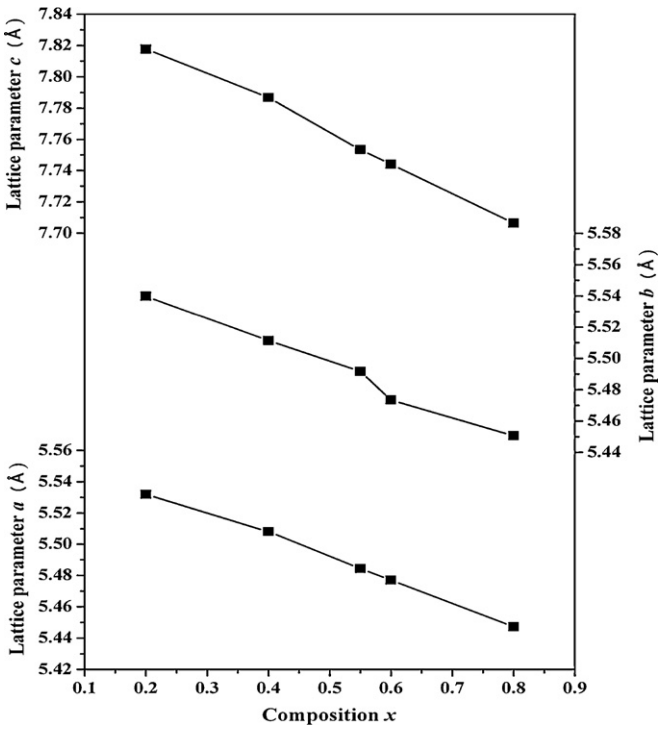

Fig. 2. The lattice parameters of the $(1-x)La(Mg_{0.5}Ti_{0.5})O_3$–$xCa_{0.8}Sm_{0.4/3}TiO_3$ solid solutions.

Fig. 3 shows the XRD patterns of the $0.45La(Mg_{0.5}Ti_{0.5})O_3$–$0.55Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics (hereafter referred to as 45LMCST) sintered at different temperatures (1380–1530 °C). It includes peaks that indicate the presence of $La(Mg_{0.5}Ti_{0.5})O_3$ and $Ca_{0.8}Sm_{0.4/3}TiO_3$ as crystalline phases. The mixed phases in the $0.45La(Mg_{0.5}Ti_{0.5})O_3$–$0.55Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramic system were formed because the structures were the same, and a solid solution system was realized. The figure reveals that a series of extra peaks was present at the (−1 1 1), (0 2 1) and (−2 1 1) positions.

The SEM images of 45LMCST ceramics sintered at different temperatures for 4 h are illustrated in Fig. 4. The result indicates that the specimen does not appear dense and the grain is not grown at 1380 °C. As the sintering temperature increases, the grain size

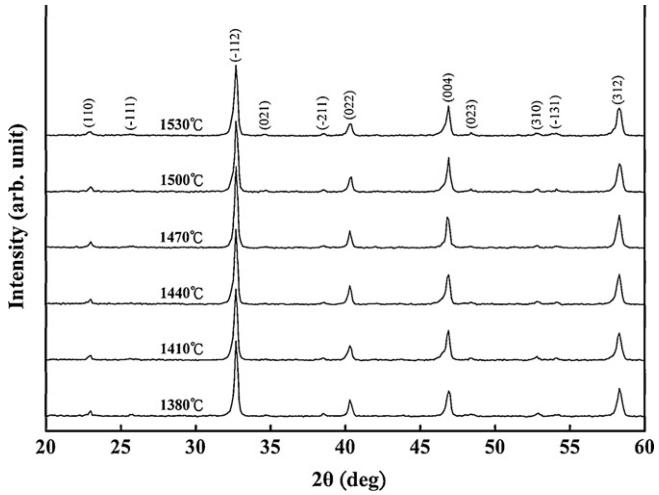

Fig. 3. X-ray diffraction patterns of $0.45La(Mg_{0.5}Ti_{0.5})O_3$–$0.55Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics sintered at different temperatures for 4 h.

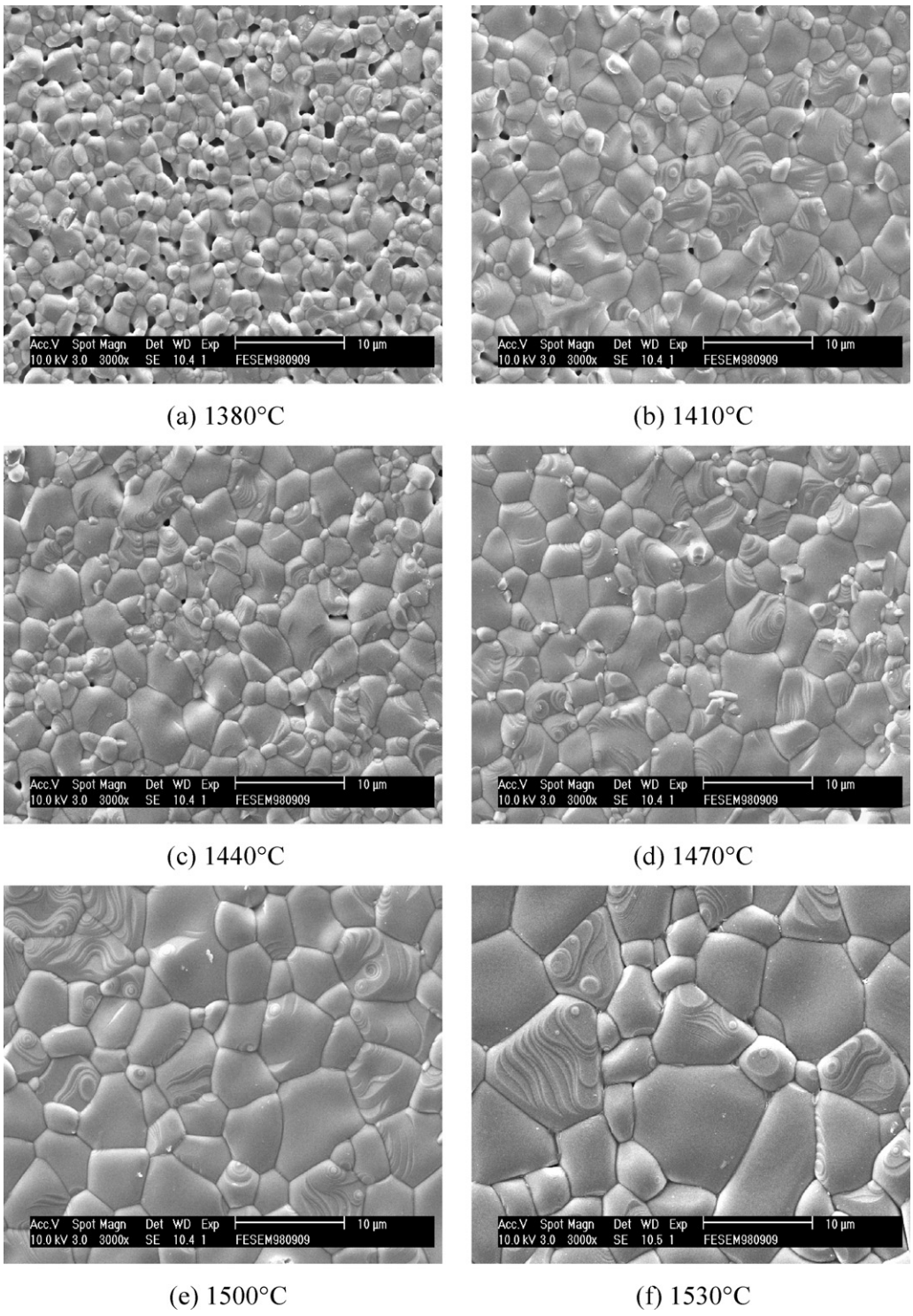

Fig. 4. SEM images of $0.45La(Mg_{0.5}Ti_{0.5})O_3$–$0.55Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics sintered at (a) 1380, (b) 1410, (c) 1440, (d) 1470, (e) 1500 and (f) 1530 °C for 4 h.

increases. The pores are almost eliminated for specimen sintered at 1440 °C, and a noticeable grain growth and a relatively uniform surface morphology are observed at 1470 °C. However, rapid grain growth is monitored at temperatures 1530 °C, which might degrade the microwave dielectric properties of the ceramics.

The apparent densities and ε_r of 45LMCST ceramics sintered at different temperatures for 4 h are shown in Fig. 5. With increasing temperature, the density increased to a maximum value of 4.86 g/cm^3 at 1470 °C, and thereafter it decreased. The lowing in the density of the specimen could be due to trapped porosity caused by the evaporation of Mg and also due to rapid grain growth as illustrated in Fig. 4. The variation of ε_r was consistent with that of density. A maximum ε_r value of 47.83 was obtained for specimen sintered at 1470 °C for 4 h.

The $Q \times f$ and τ_f values of 45LMCST ceramics sintered at different temperatures for 4 h are demonstrated in Fig. 6. By increasing the sintering temperature, the $Q \times f$ value increased to a maximum value and decreased thereafter. It showed a similar trend with that

Table 2
Comparison of microwave dielectric properties of some ceramic system.

Composition	ε_r	$Q\times f$ (GHz)	τ_f (ppm/°C)	Note
$0.5La(Mg_{0.5}Ti_{0.5})O_3$–$0.5CaTiO_3$	43	24,470	−8.94	Ref. [15]
$0.6La(Mg_{0.5}Ti_{0.5})O_3$–$0.4(La_{0.5}Na_{0.5})TiO_3$	36	25,500	−5	Ref. [17]
$0.6La(Mg_{0.5}Ti_{0.5})O_3$–$0.4(Na_{0.5}Nd_{0.5})TiO_3$	42	33,000	0.5	Ref. [18]
$0.3NdAlO_3$–$0.7CaTiO_3$	43.5	30,000	−2.1	Ref. [26]
$0.3(La_{0.5}Nd_{0.5})AlO_3$–$0.7CaTiO_3$	41.5	37,000	4	Ref. [26]
$0.45La(Mg_{0.5}Ti_{0.5})O_3$–$0.55Ca_{0.8}Sm_{0.4/3}TiO_3$	47.83	26,500	−1.7	This work

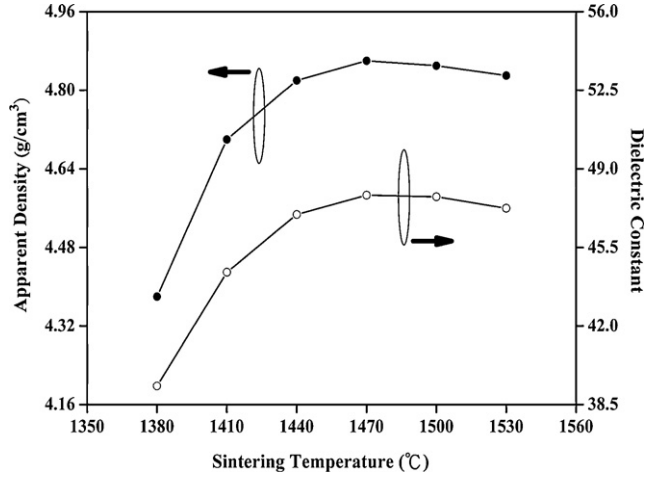

Fig. 5. Apparent density and dielectric constant of $0.45La(Mg_{0.5}Ti_{0.5})O_3$–$0.55Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics as a function of its sintering temperature.

of density suggesting that the variation of $Q\times f$ was mainly a result from its corresponding density. In addition, uniform morphology also assisted in lowering the dielectric loss. A maximum $Q\times f$ value of 26,500 GHz (at 6.2 GHz) showing a 13.7% increase compared to that of $0.5La(Mg_{0.5}Ti_{0.5})O_3$–$0.5CaTiO_3$ solid solution is obtained for the 45LMCST ceramics sintered at 1470 °C for 4 h. The degradation of $Q\times f$ is attributed to the rapid grain growth resulted in a reduction of density as observed in Fig. 4. The microwave dielectric loss is mainly caused not only by the lattice vibrational modes, but also by the pores, the second phases, the impurities or the lattice defect [23–25]. Apparent density also plays an important role in controlling the dielectric loss and has been shown for other microwave dielectric materials. Since the $Q\times f$ of 45LMCST ceramics is consistent with the variation of density, it suggests the dielectric loss

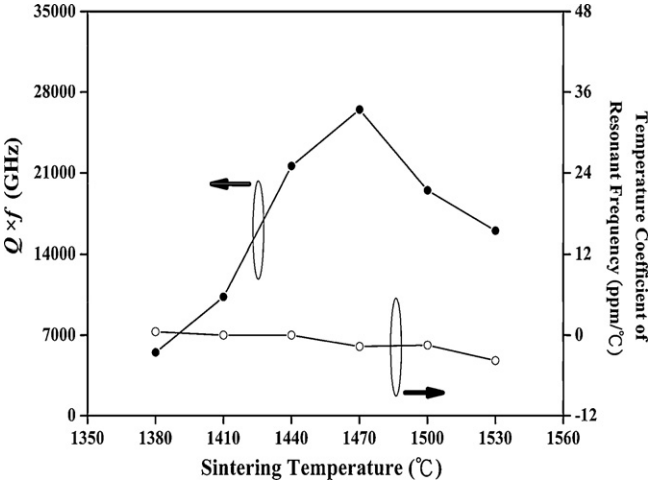

Fig. 6. $Q\times f$ and τ_f value of $0.45La(Mg_{0.5}Ti_{0.5})O_3$–$0.55Ca_{0.8}Sm_{0.4/3}TiO_3$ ceramics as a function of its sintering temperature.

of 45LMCST ceramics is mainly controlled by apparent density. In addition, uniform grain morphologies yielded maximum $Q\times f$ for specimen prepared at 1470 °C due to a reduction in lattice imperfection and dielectric loss. The temperature coefficient of resonant frequency (τ_f) is known to be governed by the composition, the additives, and the second phase of the material. As for the τ_f value, no significant change is observed throughout the experiment. This is expected since there is no compositional variation involved. At $x = 0.45$, specimen with a τ_f value of −1.7 ppm/°C is obtained.

Table 2 illustrates the microwave dielectric properties of some similar ceramic systems for comparison. The proposed dielectric possesses the highest ε_r with comparable $Q\times f$ and τ_f values. Although the Nd-contained ceramics show a higher $Q\times f$, the ε_r however is lowered. Moreover, the use of Nd_2O_3 is expensive and will certainly limit its practical applications.

4. Conclusion

Investigations on the crystal structures and the microwave dielectric properties of solid solution $(1-x)La(Mg_{0.5}Ti_{0.5})O_3$–$xCa_{0.8}Sm_{0.4/3}TiO_3$ have shown that these materials possess relatively high $Q\times f$, high dielectric constant and tunable τ_f. The microwave dielectric properties correlated to the sintering temperature and the compositional ratio of the specimens. A rapid grain growth would lead to a decrease in the density and $Q\times f$ of the ceramics. A new microwave dielectric material having high ε_r of 47.83, $Q\times f$ of 26,500 GHz (measured at 6.2 GHz) and τ_f of −1.7 ppm/°C was obtained from the compound $0.45La(Mg_{0.5}Ti_{0.5})O_3$–$0.55Ca_{0.8}Sm_{0.4/3}TiO_3$. It is proposed as a suitable candidate material for small-sized GPS patch antennas.

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References

[1] Y.B. Chen, J. Alloys Compd. 478 (2009) 781–784.
[2] G.G. Yao, P. Liu, Physica B 405 (2010) 547–551.
[3] M.S. Fu, X.Q. Liu, X.M. Chen, Y.W. Zeng, J. Am. Ceram. Soc. 91 (2008) 1163–1168.
[4] C.L. Huang, H.L. Chen, C.C. Wu, Mater. Res. Bull. 36 (2001) 1645–1652.
[5] C.L. Huang, C.F. Tseng, W.R. Yang, T.J. Yang, J. Am. Ceram. Soc. 91 (2008) 2201–2204.
[6] C.L. Huang, J.Y. Chen, J. Am. Ceram. Soc. 92 (2009) 379–383.
[7] S.Y. Cho, M.K. Seo, K.S. Hong, S.J. Park, I.T. Kim, Mater. Res. Bull. 32 (1997) 725–735.
[8] C.F. Tseng, C.L. Huang, C.H. Hsu, J. Am. Ceram. Soc. 90 (2007) 1619–1622.
[9] Y.C. Chen, Y.H. Chang, J. Alloys Compd. 477 (2009) 450–453.
[10] D.Y. Lee, S.J. Yoon, J.H. Yeo, S. Nahm, J.H. Paik, K.C. Whang, B.G. Ahn, J. Mater. Sci. Lett. 19 (2000) 131–134.
[11] H.T. Song, C.S. Hsu, M.T. Kuo, C.L. Huang, Mater. Lett. 58 (2004) 2829–2833.
[12] S.Y. Cho, C.H. Kim, D.W. Kim, K.S. Hong, J.H. Kim, J. Mater. Res. 14 (1999) 2484–2487.
[13] Y.B. Chen, J. Alloys Compd. 480 (2009) 265–269.
[14] M.P. Seabra, M. Avdeev, V.M. Ferreira, R.C. Pullar, N.M. Alford, J. Eur. Ceram. Soc. 23 (2003) 2403–2408.
[15] C.L. Huang, Y.B. Chen, C.W. Lo, Jpn. J. Appl. Phys. 44 (2005) 3147–3150.
[16] Y.B. Chen, J. Alloys Compd. 491 (2010) 330–334.
[17] Y.B. Chen, J. Alloys Compd. 496 (2010) 660–664.

[18] Y.B. Chen, J. Alloys Compd. 500 (2010) 190–194.
[19] K.H. Yoon, W.S. Kim, E.S. Kim, Mater. Sci. Eng. B99 (2003) 112–115.
[20] B.W. Hakki, P.D. Coleman, IEEE Trans. Microw. Theory Tech. 8 (1960) 402–410.
[21] W.E. Courtney, IEEE Trans. Microw. Theory Tech. 18 (1970) 476–485.
[22] R.D. Shannon, Acta Crystallogr. A32 (1976) 751–767.
[23] B.D. Silverman, Phys. Rev. 125 (1962) 1921–1930.
[24] S.J. Penn, N.M. Alford, A. Templeton, X. Wang, M. Xu, M. Reece, K. Schrapel, J. Am. Ceram. Soc. 80 (1997) 1885–1888.
[25] H. Tamura, J. Eur. Ceram. Soc. 26 (2006) 1775–1780.
[26] E.A. Nenasheva, L.P. Mudroliubova, N.F. Kartenko, J. Eur. Ceram. Soc. 23 (2003) 2443–2448.