Journal of Alloys and Compounds 509 (2011) 4247–4251

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Effect of $CaTiO_3$ addition on microwave dielectric properties of $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics

Cheng-Liang Huang*, Jhih-Yong Chen, Bing-Jing Li

Department of Electrical Engineering, National Cheng Kung University, No. 1 University Road, Tainan 70101, Taiwan

ARTICLE INFO

Article history:
Received 21 May 2010
Received in revised form 27 June 2010
Accepted 30 June 2010
Available online 7 July 2010

Keywords:
Crystal growth
Dielectric response

ABSTRACT

The microwave dielectric properties of $CaTiO_3$-added $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics prepared by the mixed oxide route have been investigated. The combination of spinel-structured $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ and perovskite-structured $CaTiO_3$ forms a two-phase system $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$xCaTiO_3$, which was confirmed by the XRD patterns and the EDX analysis and it also leads to a zero τ_f. The microwave dielectric properties of the ceramics can be effectively controlled by varying the x value. For practical applications, a new microwave dielectric material $0.91Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$0.09CaTiO_3$ is suggested and it possesses a good combination of dielectric properties with an ε_r of ~18.01, a $Q\times f$ of ~92,000 GHz, and a τ_f of ~0 ppm/°C, which makes it is a very promising candidate material for high frequency applications.

1. Introduction

The development of microwave dielectric materials for applications as substrates, resonators, filters, and patch antennas in communication systems has received much more attention in the last two decades. A material with a high dielectric constant for volume efficiency is a major requirement in modern wireless communication technology. In addition, a low-dielectric-loss for better selectivity and a near-zero temperature coefficient of resonant frequency (τ_f) for stable frequency stability is also critical requirements for practical applications [1]. However, as the carrier frequency of communication systems being extended to a higher frequency region, materials with high dielectric constant has become of less interest. Instead, high $Q\times f$ has been playing a more prominent role [2]. For instance, low-loss dielectric with different dielectric constants [3–10] has become one of the most popular materials for today's GPS patch antennas.

Mg_2TiO_4 ceramic is a low-loss and low-cost material for microwave frequency applications. It has a spinel structure belonging to the cubic space group *Fd-3m* (2 2 7) [8,11]. Moreover, it possesses a high dielectric constant ($\varepsilon_r \sim 14$), a high Q value ($Q \sim 15{,}000$ at 10 GHz), and a negative τ_f value (−50 ppm/°C) [9]. In order to produce a temperature-stable material, $CaTiO_3$ ($\tau_f \sim +800$ ppm/°C) was added to Mg_2TiO_4 and $0.93Mg_2TiO_4$–$0.07CaTiO_3$ ceramic was reported to have excellent dielectric properties with an ε_r of ~15, a $Q\times f$ of ~35,000 GHz, and a τ_f of −2 ppm/°C [9]. Still, its $Q\times f$ is insufficient for high frequency applications. Modifications on Mg_2TiO_4 ceramics were also performed to achieve a higher $Q\times f$ value. Since the ionic radius of Sn^{4+} (0.69 Å, CN = 6) is similar to that of Ti^{4+} (0.605 Å, CN = 6) [12], the Ti^{4+} ion was partially substituted by Sn^{4+} to form $Mg_2(Ti,Sn)O_4$ compositions [10]. The $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics having a spinel-type structure was reported to possess excellent microwave dielectric properties: ε_r value of 15.57, $Q\times f$ value of 317,500 GHz (at 10.8 GHz), and τ_f value of −45.1 ppm/°C [10]. Apparently, it possesses a much higher $Q\times f$ in comparison with that of pure Mg_2TiO_4. These results motivated us to study the effect of the $CaTiO_3$ addition on the dielectric properties of Mg_2TiO_4 ceramic.

In this paper, the microwave dielectric properties of the two-phase ceramic system $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$xCaTiO_3$ were investigated. The resultant microwave dielectric properties were analyzed based upon the densification, the X-ray diffraction (XRD) patterns and the microstructures of the ceramics. The correlation between the microstructure and the $Q\times f$ value was also investigated.

2. Experimental procedure

The $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ and $CaTiO_3$ powders were individually prepared from MgO, SnO_2, $CaCO_3$, and TiO_2 of >99.9% purity. The initial oxide powders were mixed and ground in an agate ball mill together with distilled water for 24 h. The wet mixtures were dried at 100 °C, thoroughly milled before they were calcined at 1100 °C for 4 h. The calcined powders were mixed according to the molar fraction $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$xCaTiO_3$ (x = 0.03–0.15). Prepared powders were dried, ball-milled for 24 h with 5 wt% of a 10% solution of PVA as a binder (Polyvinyl alcohol 500, Showa, made in Japan), granulated by sieving through 100 mesh, and pressed into pellets with 11 mm in diameter and 5 mm in thickness under the pressure of 200 MPa. These pellets were sintered at temperatures of 1210–1360 °C for 4 h in air. The heating rate and the cooling rate were both set at 5 °C/min.

The crystalline phases of the sintered ceramics were identified by XRD using Cu $K\alpha$ (λ = 0.15406 nm) radiation with a Siemens D5000 diffractometer operated at

* Corresponding author. Tel.: +886 6 2757575x62390; fax: +886 6 2345482.
E-mail address: huangcl@mail.ncku.edu.tw (C.-L. Huang).

0925-8388/$ – see front matter © 2011 Published by Elsevier B.V.
doi:10.1016/j.jallcom.2010.06.194

Table 1
Microwave dielectric properties of $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$xCaTiO_3$ ceramic system sintered at 1300 °C for 4 h.

x value	Apparent density (g/cm^3)	ε_r	$Q\times f$ (GHz)	τ_f (ppm/°C)
0.03	3.49	15.72	162,500	−35.7
0.06	3.51	16.66	116,000	−20.9
0.09	3.55	18.01	92,000	0
0.12	3.59	19.47	65,300	26.5
0.15	3.62	21.08	37,000	65.2

40 kV and 40 mA. The microstructural observations and analysis of sintered surface were performed using a scanning electron microscopy (SEM, Philips XL-40FEG) and an energy dispersive X-ray spectrometer (EDS). 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 [13,14]. A system combining a HP8757D network analyzer and a HP8350B sweep oscillator was employed in the measurement. To determine the temperature coefficient of resonant frequency (τ_f), the same technique as that of quality factor measurement was used. The test cavity was placed over a thermostat and the temperature range used was +25 to +80 °C.

3. Results and discussion

Microwave dielectric properties of $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$xCaTiO_3$ ceramic system sintered at 1300 °C for 4 h are illustrated in Table 1. Not only did the x control the ε_r and $Q\times f$ values, the τ_f was also a function of x owing to a variation in its compositional ratio. Moreover, a zero τ_f can be achieved from specimen using $0.91Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$0.09CaTiO_3$ (hereafter referred to as 91MTS–9CT).

Fig. 1 shows the XRD patterns of 91MTS–9CT ceramics sintered at different temperatures for 4 h. The XRD patterns showed that peaks indicating the presence of $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ as the main crystalline phase, in association with $CaTiO_3$ as a minor phase. Moreover, it is understood that crystal structures of $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ and $CaTiO_3$ are cubic (ICDD-PDF #00-025-1157) and orthorhombic (ICDD-PDF #00-022-0153), respectively. The X-ray diffraction patterns of the 91MTS–9CT ceramics did not change significantly with sintering temperatures in the range 1210–1360 °C. Fig. 2 shows the XRD patterns of $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$xCaTiO_3$ ceramic system at 1300 °C for 4 h. With the increase of x, $CaTiO_3$ phase gradually enhanced and a two-phase system was clearly observed.

Fig. 3 shows the change in shrinkage of $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics with various amounts of $CaTiO_3$ additions. The results illustrate that the onset temperature of shrinkage is lowered with the small addition of $CaTiO_3$ and is a function of $CaTiO_3$ content. It is noteworthy that the densification of $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics with 15 mole% $CaTiO_3$ addition begins at temperature below 1000 °C. Consequently, higher density can be achieved at lower sintering temperature for $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics with $CaTiO_3$ additions. The shrinkage curves provided more clear inspection of the contribution of $CaTiO_3$ addition to the densification of $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics.

The SEM photographs of 91MTS–9CT ceramics sintered at different temperatures for 4 h are illustrated in Fig. 4. Porous microstructure can be seen for specimen sintered at 1210 °C and the grain size increases as the sintering temperature increases due to a grain growth. Well-developed microstructure can be achieved at temperatures 1270–1300 °C and further increase in the sintering temperature would lead to an over-sintered grain morphology resulting in a rapid grain growth, which might degrade the microwave dielectric properties of the ceramics. Energy dispersive X-ray (EDX) analysis was used in combination with scanning electron microscopy to distinguish every grain for 91MTS–9CT ceramics sintered at 1300 °C, as shown in Fig. 4(d). The EDX data of corresponding Spots A–E are shown in Table 2. The grain morphology of well-developed 91MTS–9CT ceramics could be grouped into two types: large grains (Spots A–C) were $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ and small cubic-shape grains (Spots D and E) were $CaTiO_3$. The EDX evidences were in agreement with XRD results that can be obtained 91MTS–9CT ceramics.

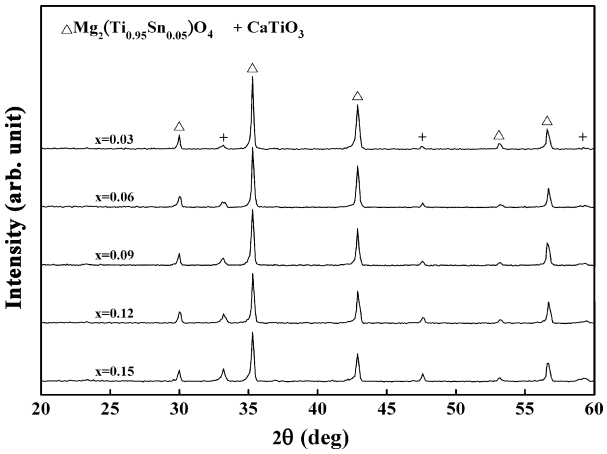

Fig. 2. X-ray diffraction patterns of $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$xCaTiO_3$ ceramic system sintered at 1300 °C for 4 h with different x values.

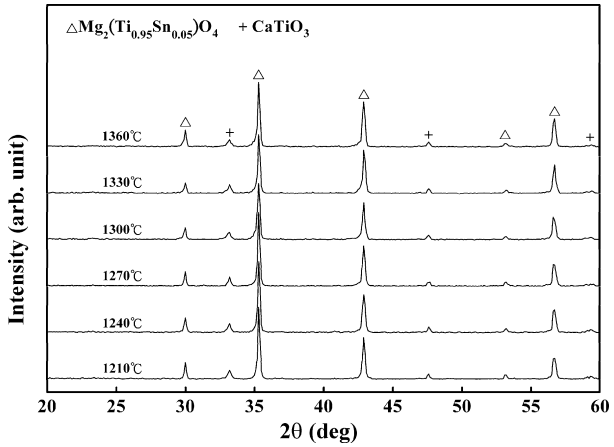

Fig. 1. X-ray diffraction patterns of $0.91Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$0.09CaTiO_3$ ceramics sintered at different temperatures for 4 h.

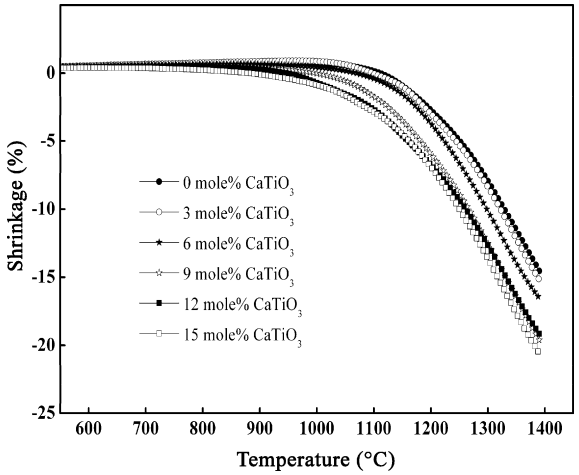

Fig. 3. Shrinkage of the $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ samples with 3–15 mole% $CaTiO_3$ additions.

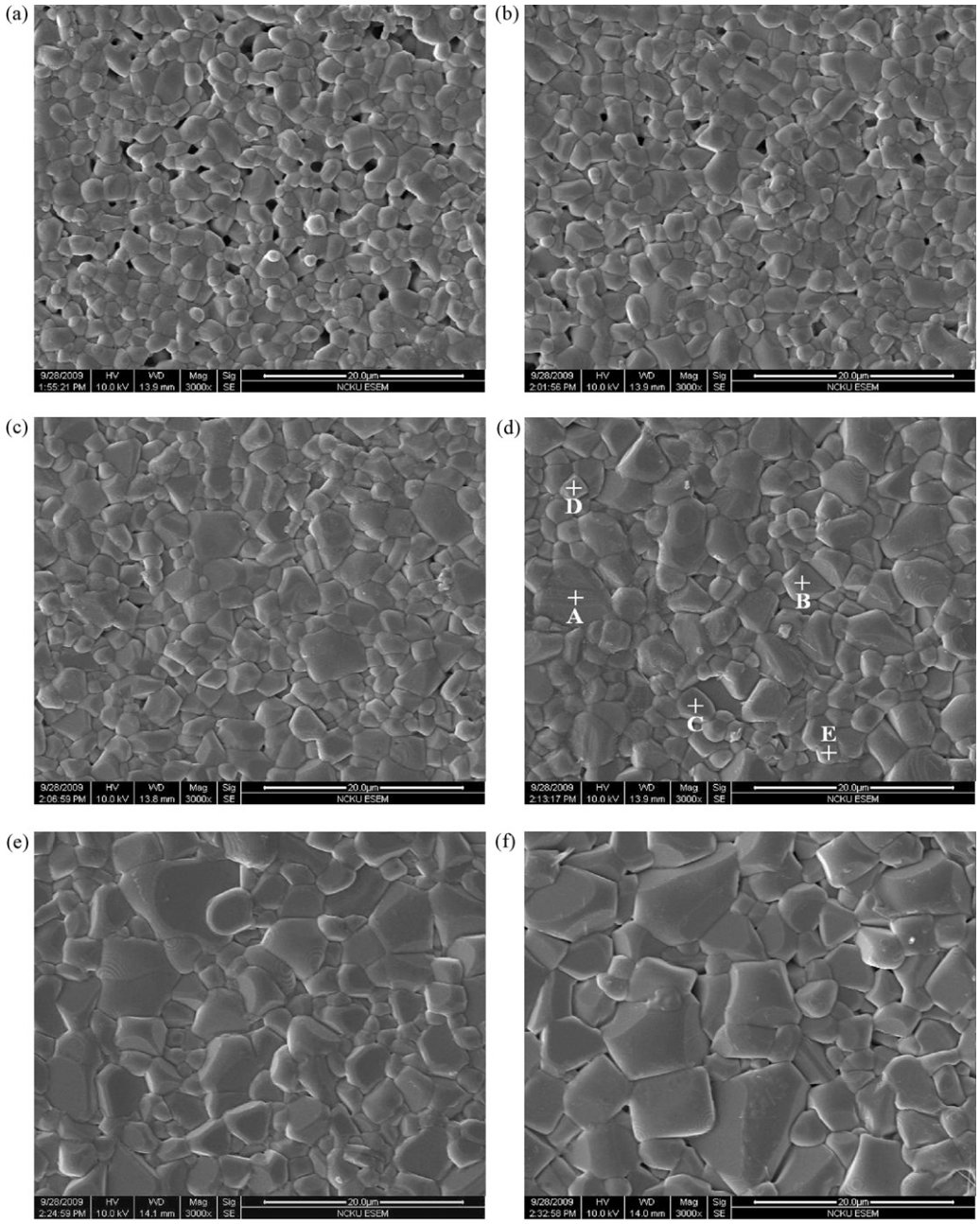

Fig. 4. SEM photographs of $0.91Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$0.09CaTiO_3$ ceramics sintered at (a) 1210 °C, (b) 1240 °C, (c) 1270 °C, (d) 1300 °C, (e) 1330 °C, and (f) 1360 °C for 4 h.

The SEM photographs of $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$xCaTiO_3$ ceramic system with different x values sintered at 1300 °C are illustrated in Fig. 5. All samples in the present study showed homogeneous grain morphology. In addition, as the x value increased, the average grain size of $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$xCaTiO_3$ ceramics decreased because $CaTiO_3$ grain is smaller than that of $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ as indicated in Fig. 4.

Table 2
The EDX data of the Spots A–E shown in Fig. 4(d).

Spots	Atom (%)				
	Mg K	Sn L	Ca K	Ti K	O K
A	29.81	0.98	0	15.66	53.55
B	30.52	0.85	0	16.03	52.60
C	31.17	0.97	0	14.94	52.92
D	0	0	20.38	20.02	59.60
E	0	0	20.27	20.75	58.98

Fig. 6 shows the apparent densities of 91MTS–9CT ceramics sintered at different temperatures for 4 h. With increasing sintering temperature, the apparent density of 91MTS–9CT increased to a maximum value of 3.55 g/cm^3 at 1300 °C and thereafter it decreased. Moreover, the degradation of apparent density at high temperatures was owing to the rapid grain growth as observed in Fig. 4.

The dielectric constant of 91MTS–9CT ceramics sintered at different temperatures for 4 h is illustrated in Fig. 7. Variation of dielectric constant was consistent with that of density. The dielectric constant of 91MTS–9CT initially increased with increasing sintering temperature. After reaching the maximum at 1300 °C, it decreased. A maximum ε_r value of 18.01 was obtained for 91MTS–9CT ceramics sintered at 1300 °C for 4 h. It indicates further

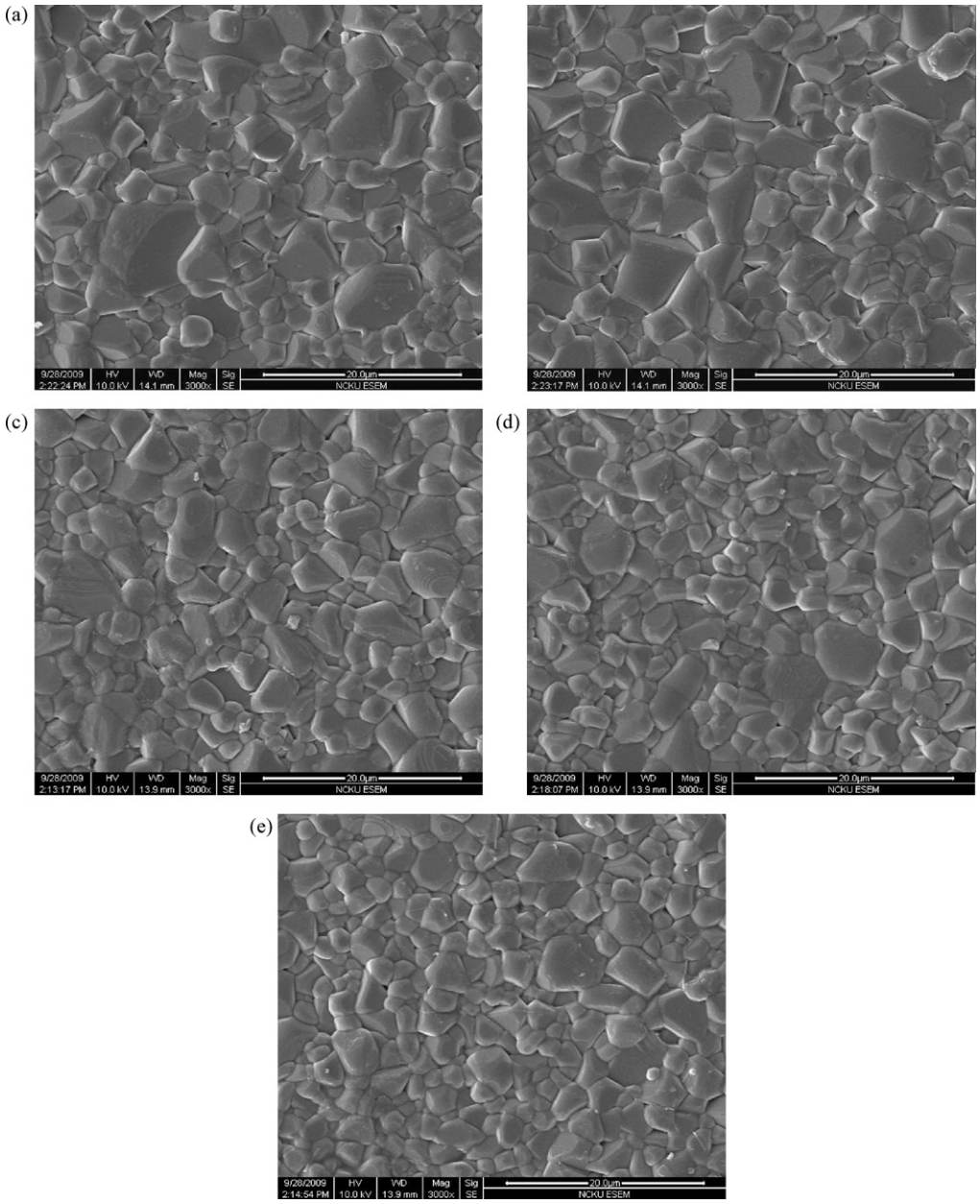

Fig. 5. SEM photographs of the $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$xCaTiO_3$ ceramic system with x = (a) 0.03, (b) 0.06, (c) 0.09, (d) 0.12, and (e) 0.15 sintered at 1300 °C for 4 h.

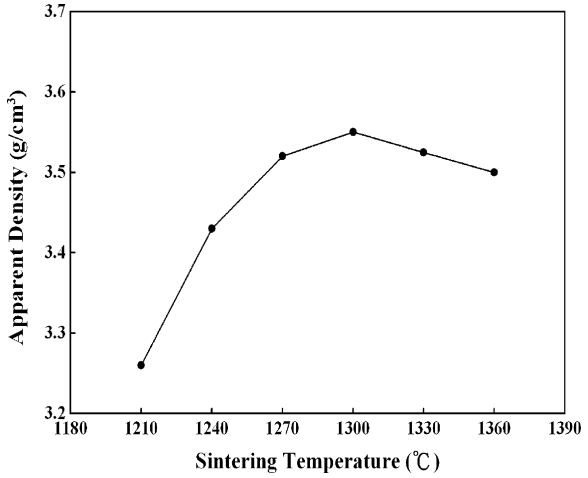

Fig. 6. Apparent density of $0.91Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$0.09CaTiO_3$ ceramics as a function of its sintering temperature.

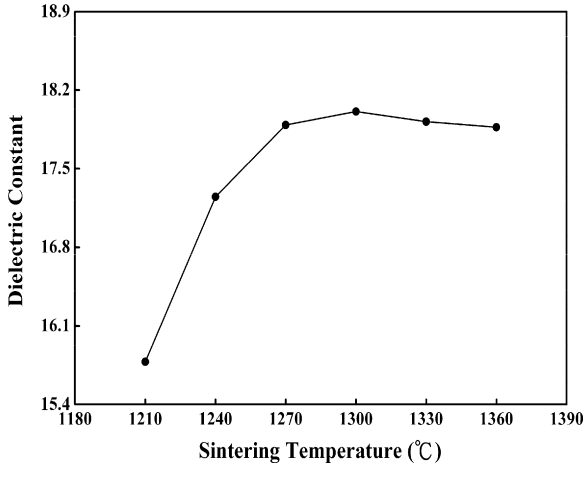

Fig. 7. Dielectric constant of $0.91Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$0.09CaTiO_3$ ceramics as a function of its sintering temperature.

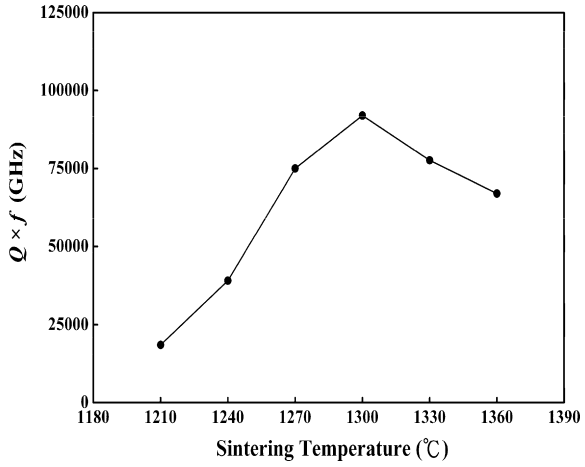

Fig. 8. $Q \times f$ value of $0.91Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$0.09CaTiO_3$ ceramics as a function of its sintering temperature.

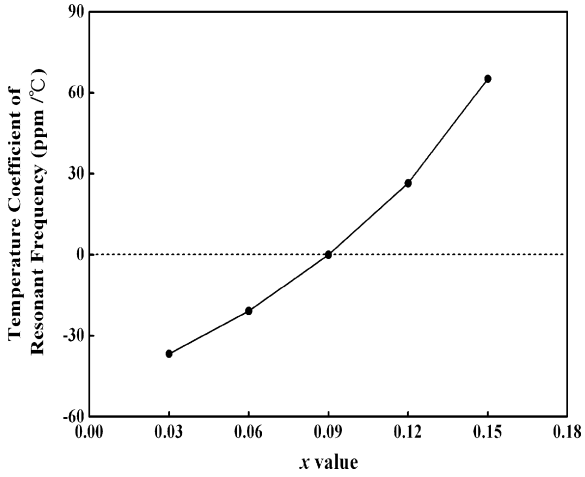

Fig. 9. τ_f value of $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$xCaTiO_3$ ceramic system sintered at 1300 °C for 4 h with different x values.

increase in the sintering temperature does not certainly lead to a higher dielectric constant.

The $Q \times f$ of 91MTS–9CT ceramics sintered at different temperatures for 4 h are demonstrated in Fig. 8. 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 [15–17]. Apparent density also plays an important role in controlling the dielectric loss and which has been shown for other microwave dielectric materials. Since the variation of $Q \times f$ was also consistent with that of density, it suggested the dielectric loss of 91MTS–9CT ceramics was mainly controlled by the apparent density. A maximum $Q \times f$ value of 92,000 GHz (at 9.8 GHz) could be achieved for specimen using 91MTS–9CT ceramics sintered at 1300 °C for 4 h. The decrease of $Q \times f$ value was attributed to the rapid grain growth resulting in a reduction in the density as observed in Figs. 4 and 6.

Fig. 9 illustrates the temperature coefficients of resonant frequency (τ_f) of $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$xCaTiO_3$ ceramic system sintered at 1300 °C for 4 h with different x values. The temperature coefficient of resonant frequency is well known to be governed by the composition, the additives, and the second phase of the materials. By increasing $CaTiO_3$, the τ_f value almost linearly varied toward positive direction. This is because adding $CaTiO_3$ renders a large positive τ_f value (+800 ppm/°C). Through appropriate adjustment, a zero τ_f can be obtained for 91MTS–9CT specimen at 1300 °C for 4 h.

4. Conclusion

$(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$xCaTiO_3$ ($x = 0.03$–0.15) ceramic system showed mixed phases of $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ as the main phase in association with a minor phase $CaTiO_3$. The microwave dielectric properties are strongly related to the density and the matrix of the specimen. With $x = 0.09$, a zero τ_f value can be obtained for $(1-x)Mg_2(Ti_{0.95}Sn_{0.05})O_4$–$xCaTiO_3$ ceramic system. A dielectric constant ε_r of 18.01, a $Q \times f$ value of 92,000 GHz (measured at 9.8 GHz), and a τ_f value of 0 ppm/°C were obtained for 91MTS–9CT ceramics sintered at 1300 °C for 4 h. As a result, 91MTS–9CT is a very promising dielectric for applications as microwave dielectric resonators, filters and patch antennas due to its excellent microwave dielectric properties.

Acknowledgement

This work was supported by the National Science Council of Taiwan under grant NSC 97-2262-E-006-013-MY3.

References

[1] C.L. Huang, C.F. Tseng, W.R. Yang, T.J. Yang, J. Am. Ceram. Soc. 91 (2008) 2201–2204.
[2] C.L. Huang, J.J. Wang, Y.P. Chang, J. Am. Ceram. Soc. 90 (2007) 858–862.
[3] B.L. Liang, X.H. Zheng, D.P. Tang, J. Alloys Compd. 488 (2009) 409–413.
[4] C.H. Hsu, Y.S. Chang, J. Alloys Compd. 479 (2009) 714–718.
[5] L. Fang, H. Su, Q. Yu, H. Zhang, B. Wu, J. Am. Ceram. Soc. 9 (2008) 2769–2771.
[6] C.L. Huang, J.Y. Chen, J. Am. Ceram. Soc. 93 (2010) 470–473.
[7] C.L. Huang, J.Y. Chen, B.J. Li, J. Alloys Compd. 484 (2009) 494–497.
[8] A. Belous, O. Ovchar, D. Durylin, M. Valant, M.M. Krzmanc, D. Suvorov, J. Eur. Ceram. Soc. 27 (2007) 2963–2966.
[9] A. Belous, O. Ovchar, D. Durilin, M.M. Krzmanc, M. Valant, D. Suvorov, J. Am. Ceram. Soc. 89 (2006) 3441–3445.
[10] C.L. Huang, J.Y. Chen, J. Am. Ceram. Soc. 92 (2009) 2237–2241.
[11] M. Isobe, Y. Ueda, J. Alloys Compd. 383 (2004) 85–88.
[12] R.D. Shannon, Acta Cryst. A32 (1976) 751–767.
[13] B.W. Hakki, P.D. Coleman, IEEE Trans. Microwave Theory Tech. 8 (1960) 402–410.
[14] W.E. Courtney, IEEE Trans. Microwave Theory Tech. 18 (1970) 476–485.
[15] B.D. Silverman, Phys. Rev. 125 (1962) 1921–1930.
[16] S.J. Penn, N.M. Alford, A. Templeton, X. Wang, M. Xu, M. Reece, K. Schrapel, J. Am. Ceram. Soc. 80 (1997) 1885–1888.
[17] H. Tamura, J. Eur. Ceram. Soc. 26 (2006) 1775–1780.