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Dielectric properties of $(1-x)(Mg_{0.95}Co_{0.05})TiO_3$–$xCaTiO_3$ ceramic system at microwave frequency

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Abstract

The microwave dielectric properties and the microstructures of the $(1-x)MgTiO_3$–$xCaTiO_3$ ceramic system were investigated. With partial replacement of Mg by Co, dielectric properties of the $(1-x)(Mg_{0.95}Co_{0.05})TiO_3$–$xCaTiO_3$ ceramics can be promoted. The microwave dielectric properties are strongly correlated with the sintering temperature. At 1275°C, the $0.95(Mg_{0.95}Co_{0.05})TiO_3$–$0.05CaTiO_3$ ceramics possesses excellent microwave dielectric properties: a dielectric constant ε_r of 20.3, a $Q \times f$ value of 107 000 (at 7 GHz) and a τ_f value of −22.8 ppm/°C. By appropriately adjusting the x value in the $(1-x)(Mg_{0.95}Co_{0.05})TiO_3$–$xCaTiO_3$ ceramic system, zero τ_f value can be achieved. With $x = 0.07$, a dielectric constant ε_γ of 21.6, a $Q \times f$ value of 92 000 (at 7 GHz) and a τ_f value of −1.8 ppm/°C was obtained for $0.93(Mg_{0.95}Co_{0.05})TiO_3$–$0.07CaTiO_3$ ceramics sintered at 1275°C for 4 h.

Keywords: A. Ceramics; A. Oxides; C. X-ray diffraction; D. Dielectric properties

1. Introduction

The developments of microwave dielectric resonator and antenna for communication systems such as cellular phones and global positioning systems have been rapidly growing in the past decade [1,2]. An advantage of using dielectric materials is the possible size reduction of microwave components. Requirements for these

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dielectric materials must be the combined dielectric properties of a high dielectric constant (ε_r), a low dielectric loss (high $Q \times f$ value) and a near-zero temperature coefficient of resonant frequency (τ_f) as small as possible. These three parameters are correlated to the size, frequency selectivity and temperature stability of the system, respectively. To satisfy the demands of microwave circuit designs, each dielectric property should be precisely controlled.

$MgTiO_3$-based ceramics have wide applications as dielectrics in resonators, filters and antennas for communication, radar and global positioning systems operating at microwave frequencies. $MgTiO_3$–$CaTiO_3$ (hereafter referred to as MCT) ceramics is well known as the material for temperature compensating type capacitor, dielectric resonator and patch antenna. The material is made of a mixture of modified α-Al_2O_3 tructured magnesium titanate ($MgTiO_3$: $\varepsilon_r \sim 17$, $Q \times f$ value ~160 000 at 7 GHz and a zero τ_f value) [3] and perovskite structured calcium titanate ($CaTiO_3$: $\varepsilon_r \sim 170$, $Q \times f$ value ~3600 at 7 GHz and τ_f value ~800 ppm/°C) [4]. With the ratio Mg:Ca = 95:5, $0.95MgTiO_3$–$0.05CaTiO_3$ (hereafter referred to as 95MCT) ceramics gives $\varepsilon_r \sim 21$, $Q \sim 8000$ at 7 GHz, and a zero τ_f value. However, it required sintering temperatures as high as 1400–1450°C. Many researchers made effort to study the microstructures and the microwave dielectric properties of the 95MCT ceramics by adding various additives or varying the processing. The dielectric properties of 95MCT ceramics can be further improved by introducing additions such as Cr, La or B [5–8], although some of the τ_f values were not reported. MCT ceramics prepared by a chemical route were sintered at lower temperature and gave excellent dielectric properties ($\varepsilon_r \sim 19.1$, $Q \times f$ value ~84 800 at 8 GHz, τ_f value: unreported). However, the chemical process often required an expensive and time-consuming flexible process. With partial replacement of Mg by Co, the $(Mg_{0.95}Co_{0.05})TiO_3$ ceramics having an ilmenite-type structure was reported to possess excellent dielectric properties with an ε_r value ~16.8, a $Q \times f$ value ~23 000 at 10 GHz and a τ_f value ~ -54 ppm/°C [9]. In this paper, $CaTiO_3$ was added to $(Mg_{0.95}Co_{0.05})TiO_3$ as a ceramic system of $(1-x)(Mg_{0.95}Co_{0.05})$-$TiO_3$–$x$$CaTiO_3$, which demonstrated an effective compensation in its τ_f value. 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.

1.1. Experimental procedure

Samples of $(Mg_{0.95}Co_{0.05})TiO_3$ and $CaTiO_3$ were individually synthesized by conventional solid-state methods from high-purity oxide powders (>99.9%): MgO, CoO, $CaCO_3$ and TiO_2. The starting materials were mixed according to the stoichiometry: $(Mg_{0.95}Co_{0.05})TiO_3$ and $CaTiO_3$ and ground in distilled water for 10 h in a ball mill with agate balls. Both mixtures were dried and calcined at 1100°C for 4 h. The calcined reagents were mixed as desired composition $(1-x)(Mg_{0.95}Co_{0.05})$–$x$$CaTiO_3$ and ground into fine powder for 24 h. The fine powder together with the organic binder were forced through a 50-mesh sieve and pressed into pellets with dimensions of 11 mm in diameter and 5 mm in thickness. These pellets were sintered at temperatures of 1250–1350°C for 4 h in air. The heating rate and the cooling rate were both set at 10°C/min.

The densities of the sintered ceramics were measured using the Archimedes method. The crystalline phases were analyzed by means of the X-ray powder diffraction method using Cu Kα radiation from 20 to 60° in 2θ. The scanning rate was 4 degree/min. The microstructure was observed using a scanning electron microscope (SEM). The dielectric constants and the unloaded Q values were measured by employing the Hakki–Coleman dielectric resonator method as modified and improved by Kobayashi–Katoh [10,11]. The apparatus consisted of parallel conducting brass plates and coaxial probes connected to a HP8510B network analyzer and a HP8350B sweep oscillator. Identical technique was applied in measuring the temperature coefficient of resonant frequency (τ_f). The test set was placed over a thermostat in the temperature range from 25 to 80°C. The τ_f value (ppm/°C) can be calculated by noting the change in resonant frequency (Δf):

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

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

2. Results and discussion

Fig. 1 shows the XRD patterns of $0.95(Mg_{0.95}Co_{0.05})TiO_3$–$0.05CaTiO_3$ (hereafter referred to as 95MCCT) ceramics at different sintering temperatures. The XRD

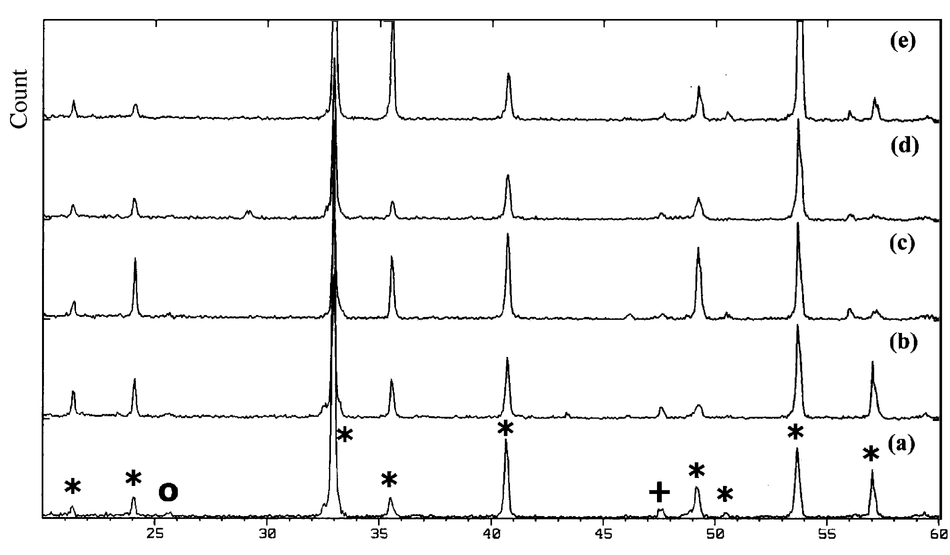

Fig. 1. X-ray diffraction patterns of $0.95(Mg_{0.95}Co_{0.05})TiO_3$–$0.05CaTiO_3$ ceramics sintered at: (a) 1250°C; (b) 1275°C; (c) 1300°C; (d) 1325°C; and (e) 1350°C for 4 h. (*) $MgTiO_3$; (+) $CaTiO_3$; (○) $MgTi_2O_5$.

patterns showed that peaks indicating the presence of $MgTiO_3$ as the main crystalline phase, in association with $CaTiO_3$ and $MgTi_2O_5$ as minor phases. It also indicated a complete solid solution for the 95MCCT ceramics. The formation of $CaTiO_3$ in 95MCT ceramics was due to the structure difference and the larger ionic size difference between Ca^{2+} (0.99 Å) and Mg^{2+}(0.65 Å). $MgTi_2O_5$, usually formed as an intermediate phase, was identified and difficult to completely eliminate from the sample prepared by mixed oxide route. The formation of $MgTi_2O_5$ might lower the $Q \times f$ value of the specimen. Similar results of the XRD pattern were obtained for $(1-x)(Mg_{0.95}Co_{0.05})TiO_3$–$x$$CaTiO_3$ ceramic system with $x = 0.06$, 0.07 and 0.08.

The SEM photographs of 95MCCT ceramics at different sintering temperatures for 4 h are illustrated in Fig. 2. The 95MCCT ceramics was not dense and the grain did not grow at 1200°C. As the sintering temperature increased, the grain size increased. The pores were almost eliminated for specimen sintered at 1250°C and the grain growth rapidly increased above 1250°C. However, inhomogeneous grain growth was observed at temperatures higher than 1270°C, which might degrade the microwave dielectric properties of the ceramics. The needle shape grains were identified, in Fig. 3, as a second phase $MgTi_2O_5$ (Mg:Ti = 1:2), which would lead to a degradation in dielectric properties.

Fig. 4 shows the bulk densities of 95MCCT ceramics at different sintering temperatures for 4 h. With increasing sintering temperature, the bulk density was found to increase to a maximum value of 3.9 g/cm^3 at 1275°C and thereafter decreased. Moreover, the degradation of bulk density at temperatures above 1275°C was owing to abnormal grain growth.

Fig. 5 shows the dielectric constants of 95MCCT ceramics at different sintering temperatures for 4 h. The relationships between ε_r values and sintering temperatures revealed the same trend with those between densities and sintering temperatures since higher density means lower porosity. The dielectric constant slightly increased with increasing sintering temperature. After reaching maximum at 1275°C, it decreased. A maximum ε_r value of 20.3 was obtained for 95MCCT ceramics sintered at 1275°C for 4 h. Increasing sintering temperature does not necessary lead to a higher dielectric constant.

The quality factor values ($Q \times f$) of 95MCCT ceramics at different sintering temperatures for 4 h are demonstrated in Fig. 6. With increasing sintering temperature, the $Q \times f$ value was found to increase to a maximum value and thereafter decreased. A maximum $Q \times f$ value of 107 000 (GHz) was obtained for 95MCCT ceramics at 1275°C. The degradation of $Q \times f$ value was attributed to inhomogeneous grain growth resulted in a reduction of density as observed in Figs. 2 and 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. Relative density also plays an important role in controlling the dielectric loss, and has been shown for other microwave dielectric materials. Since the $Q \times f$ value of 95MCCT ceramics was consistent with the variation of density, it suggested the dielectric loss of 95MCCT ceramics was mainly controlled by the bulk density. As comparing to pure

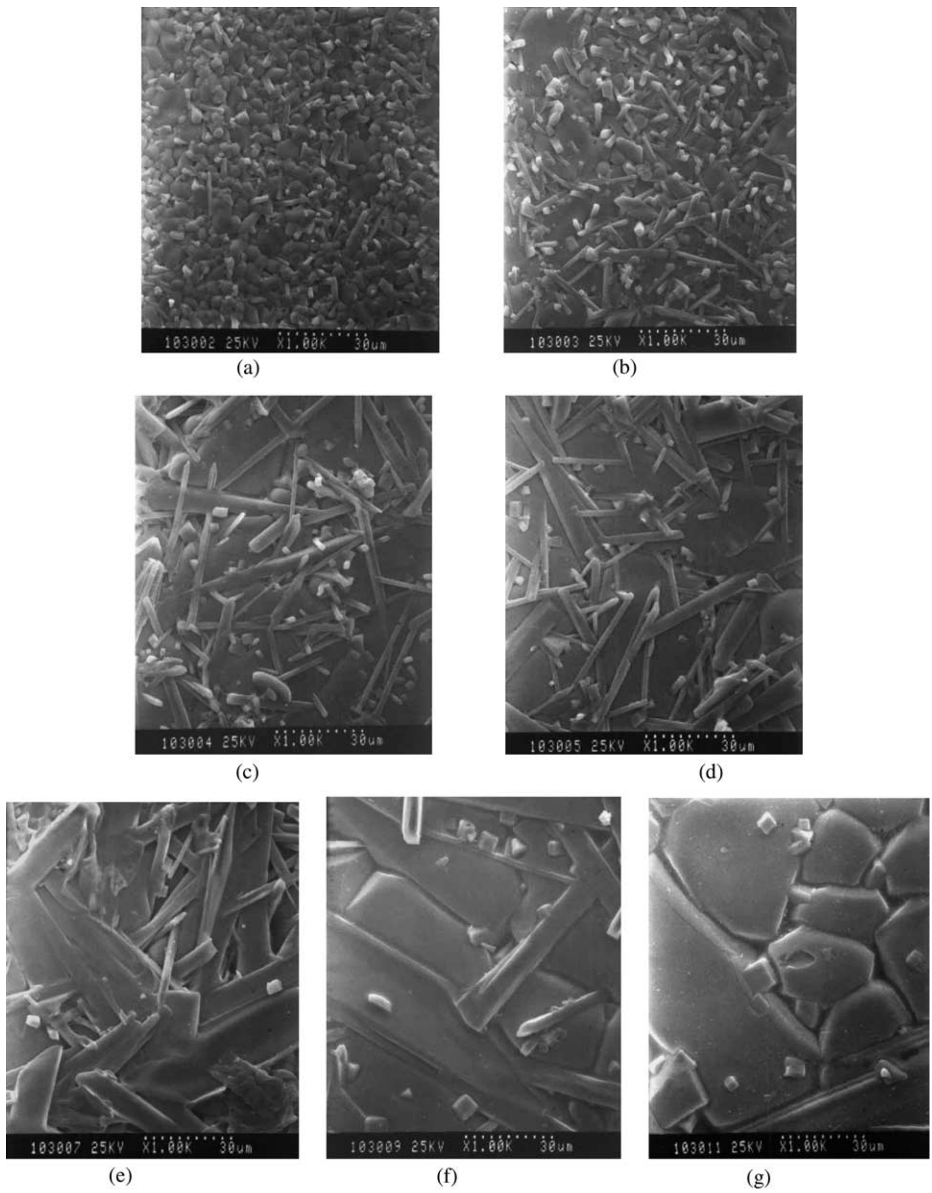

Fig. 2. SEM micrographs of $0.95(Mg_{0.95}Co_{0.05})TiO_3$–$0.05CaTiO_3$ ceramics sintered at: (a) 1200°C; (b) 1225°C; (c) 1250°C; (d) 1275°C; (e) 1300°C; (f) 1325°C; and (g) 1350°C for 4 h.

95MCT ceramics sintered at 1400°C [3], 95MCCT ceramics possessed higher $Q \times f$ values.

Fig. 7 illustrates the temperature coefficients of resonant frequency (τ_f) of 95MCCT ceramics at different sintering temperatures. Significant change was not observed in the τ_f value at different sintering temperatures. A τ_f value of −22.8 ppm/°C was obtained for 95MCCT ceramics at 1275°C for 4 h. Since the τ_f values of

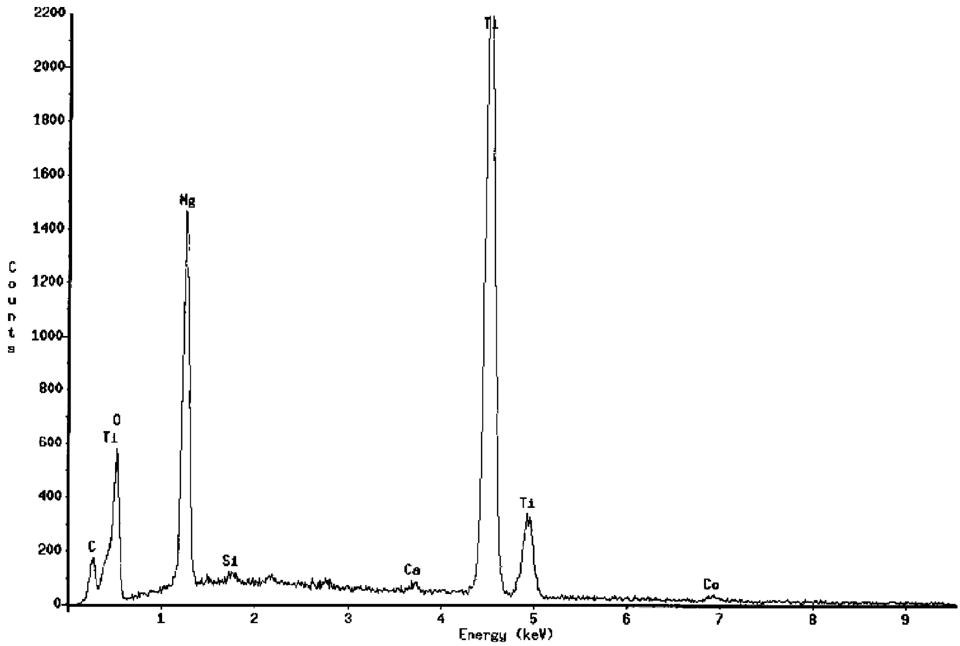

Fig. 3. EDS of needle shape grains illustrated in Fig. 2.

$(Mg_{0.95}Co_{0.05})TiO_3$ and $CaTiO_3$ are -54 and 800 ppm/°C [4,8], respectively, it implies that zero τ_f can be achieved by increasing the amount of $CaTiO_3$ content.

Table 1 demonstrates the microwave dielectric properties of $(1-x)(Mg_{0.95}Co_{0.05})$-$TiO_3$–$xCaTiO_3$ ceramic system sintered at 1275°C for 4 h. As the x value increased from 0.05 to 0.08, the τ_f values of $(1-x)(Mg_{0.95}Co_{0.05})TiO_3$–$xCaTiO_3$ ceramics varied from -22.8 to 5.4. Since the τ_f curves went through zero, it indicates that zero τ_f value can be obtained by appropriately adjusting the x value of $(1-x)$-$(Mg_{0.95}Co_{0.05})TiO_3$–$xCaTiO_3$ ceramics.

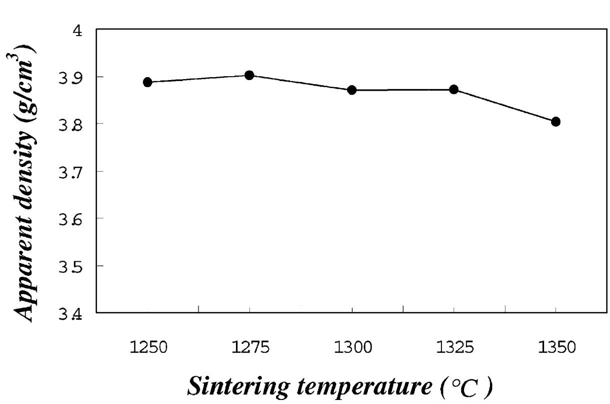

Fig. 4. Apparent density of $0.95(Mg_{0.95}Co_{0.05})TiO_3$–$0.05CaTiO_3$ ceramics as a function of its sintering temperature.

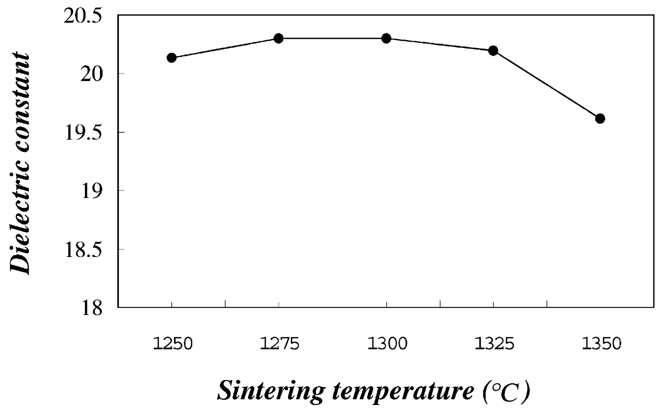

Fig. 5. ε_{γ} value of $0.95(Mg_{0.95}Co_{0.05})TiO_3$–$0.05CaTiO_3$ ceramics as a function of its sintering temperature.

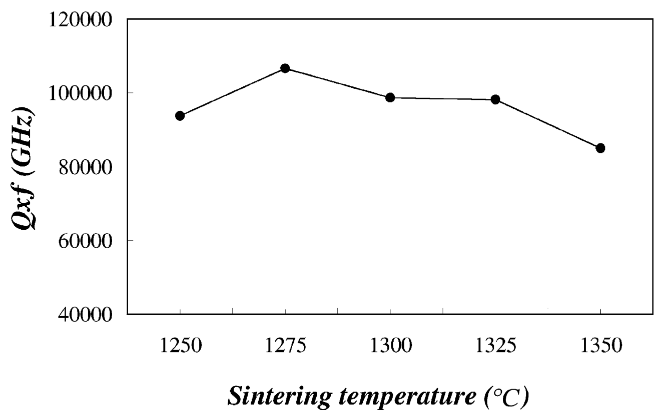

Fig. 6. $Q \times f$ value of $0.95(Mg_{0.95}Co_{0.05})TiO_3$–$0.05CaTiO_3$ ceramics as a function of its sintering temperature.

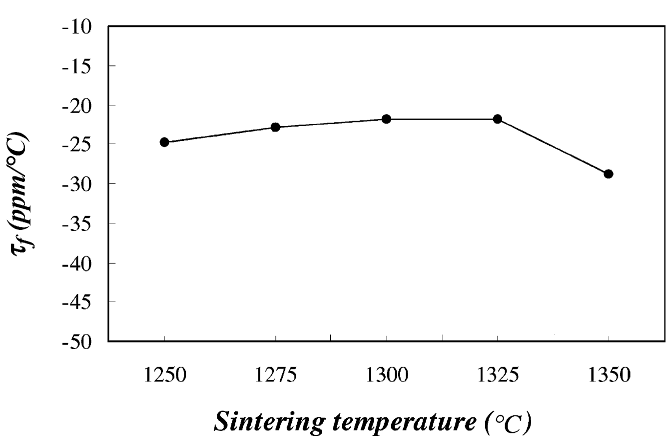

Fig. 7. τ_f value of $0.95(Mg_{0.95}Co_{0.05})TiO_3$–$0.05CaTiO_3$ ceramics as a function of its sintering temperature.

Table 1
Microwave dielectric properties of $(1-x)(Mg_{0.95}Co_{0.05})TiO_3$–$xCaTiO_3$ ceramic system sintered at 1275°C for 4 h

x value	ε_r	$Q \times f$ (at 7 GHz)	τ_f (ppm/°C)
0.00	14.3	128000	−51.1
0.05	20.3	107000	−22.8
0.06	20.9	102000	−9.5
0.07	21.6	92000	−1.8
0.08	22.1	86400	5.4

3. Conclusion

Comparing to pure 95MCT, the 95MCCT ceramics effectively promoted its dielectric properties at microwave frequency. $(1-x)(Mg_{0.95}Co_{0.05})TiO_3$–$xCaTiO_3$ ceramics showed mixed phases of $MgTiO_3$ as the main phase in association with some minor phases $CaTiO_3$ and $MgTi_2O_5$. The existence of $MgTi_2O_5$ phase would cause a decrease in the $Q \times f$ value. The microwave dielectric properties are strongly related to the density and the matrix of the specimen. A dielectric constant ε_γ of 20.3, a $Q \times f$ value of 107 000 (at 7 GHz) and a τ_f value of -22.8 ppm/°C was obtained for 95MCCT sintered at 1275°C for 4 h. Zero τ_f value can be approached by properly adjusting the x value of $(1-x)(Mg_{0.95}Co_{0.05})TiO_3$–$xCaTiO_3$ ceramics. At 1275°C, $0.93(Mg_{0.95}Co_{0.05})TiO_3$–$0.07CaTiO_3$ ceramics was found to possess excellent microwave dielectric properties: $\varepsilon_r \sim 21.6$, $Q \times f$ value ~92 000 (at 7 GHz) and τ_f value ~ -1.8 ppm/°C.

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References

[1] W. Wersing, in: B.C.H. Steele (Ed.), Electronic Ceramics, Elsevier, London, 1991, p. 67.
[2] G. Wolfram, H.E. Gobel, Mater. Res. Bull. 16 (1981) 1455.
[3] K. Wakino, Ferroelectric 91 (1989) 69.
[4] R.C. Kell, A.C. Greenham, G.C.E. Olds, J. Am. Ceram. Soc. 56 (1973) 352.
[5] V.M. Ferreira, F. Azough, I.L. Baptista, R. Freer, Ferroelectric 133 (1992) 127.
[6] V.M. Ferreira, F. Azough, R. Freer, J.L. Baptista, J. Mater. Res. 12 (1997) 3293.
[7] V.M. Ferreira, J.L. Baptista, S. Kamba, J. Petzelt, J. Mater. Soc. 28 (1993) 5894.
[8] C.L. Huang, M.H. Weng, Mater. Res. Bull. 36 (2001) 2741.
[9] J.H. Sohn, Y. Inaguma, S.O. Yoon, M. Itoh, T. Nakamura, S.J. Yoon, H.J. Kim, Jpn. J. Appl. Phys. 33 (1994) 5466.
[10] B.W. Hakki, P.D. Coleman, IEEE Trans. Microwave Theory Tech. 8 (1960) 402.
[11] Y. Kobayashi, M. Katoh, IEEE Trans. Microwave Theory Tech. 33 (1985) 586.