Journal of Alloys and Compounds 472 (2009) 451–455

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Microwave dielectric properties and sintering behaviors of $(Mg_{0.95}Ni_{0.05})TiO_3$–$CaTiO_3$ ceramic system

Chun-Hsu Shen, Cheng-Liang Huang *

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

ARTICLE INFO

Article history:
Received 4 February 2008
Received in revised form 20 April 2008
Accepted 24 April 2008
Available online 17 June 2008

Keywords:
Crystal growth
Dielectric response

ABSTRACT

The microwave dielectric properties and sintering behaviors of the new ceramic system $(1-x)(Mg_{0.95}Ni_{0.05})TiO_3$–$xCaTiO_3$ ($x \le 0.1$) prepared by conventional solid state route were investigated. The compositions with $x = 0.02$–0.1 resulted in the mixture of two main phases, $(Mg_{0.95}Ni_{0.05})TiO_3$ and $CaTiO_3$, and a second phase $(Mg_{0.95}Ni_{0.05})Ti_2O_5$, which was favorable at high temperatures. The two-phased system was confirmed by both XRD and EDS analysis. Zero τ_f can be achieved by appropriately adjusting the compositional ratio. Specimen with $x = 0.06$ possessed an excellent combination of microwave dielectric properties: $\varepsilon_r \sim 20.8$, $Q \times f \sim 79{,}200$ GHz and $\tau_f \sim 1.2$ ppm/°C. It is proposed as a candidate material for GPS patch antennas and ISM band filters.

1. Introduction

Regarding materials for microwave use, requirements for these candidates must satisfy three major criteria: a high dielectric constant for component size reduction, a low dielectric loss for high selectivity and a near-zero temperature coefficient of resonant frequency (τ_f) for stable frequency stability. However, increasing the carrier frequencies from 900 MHz to 2.4, 5.2, 5.8 GHz or even to millimeter regime, would render materials with high dielectric constant a less of interest. Low dielectric loss, on the other hand, would play a more prominent role instead. For instance, low loss dielectrics with dielectric constants in the 20 s have become most popular materials used for today's GPS patch antennas, Wireless LAN and 5.8 GHz ISM band filters [1,2]. Still, zero τ_f remains as one of the primary requirements for high frequency materials and becomes more and more critical as the operating frequency going higher.

Two conventional approaches are usually employed in the development of excellent dielectric ceramics; one is to create a new material and the other one is to combine two or more materials to achieve characteristic compensation. The latter one, mixing two or more compositions with different dielectric properties, is more popular due to its simplicity. In other words, combining two compounds having negative and positive τ_f values to form a solid solution or mixed phases is the most convenient and promising way to achieve a zero τ_f [3,4].

The ilmenite-type structured $MgTiO_3$, belonging to the trigonal space group $R\bar{3}$, is one of the leading dielectric materials for microwave applications. At microwave frequency range, it exhibits a good quality factor $Q \times f \sim 160{,}000$ at 8 GHz, a dielectric constant $\varepsilon_r \sim 17$, and a temperature coefficient of resonant frequency $\tau_f \sim -50$ ppm/°C [5]. $MgTiO_3$-based ceramics has been widely applied as dielectric materials for resonators, filters and antennas for communication, radar, and global positioning systems operated at microwave frequencies. For instance, $0.95MgTiO_3$–$0.05CaTiO_3$ ceramic is well known as the material ($\varepsilon_r \sim 20$, $Q \times f \sim 56{,}000$ GHz and a zero τ_f [5]) for temperature compensating type capacitor, dielectric resonator and patch antenna. With partial replacement of Mg by Ni, $(Mg_{0.95}Ni_{0.05})TiO_3$ (hereafter referred to as MNT) ceramic with a ilmenite-type structure was reported to possess a better combination of dielectric properties ($\varepsilon_r \sim 17.2$, $Q \times f \sim 180{,}000$ GHz, $\tau_f \sim -45$ ppm/°C) [6]) in comparison with that of $MgTiO_3$. That makes it a good candidate as a dielectric material for microwave applications.

In this paper, $CaTiO_3$ (hereafter referred to as CT) was added to $(Mg_{0.95}Ni_{0.05})TiO_3$ to form a new ceramic system $(1-x)(Mg_{0.95}Ni_{0.05})TiO_3$–$xCaTiO_3$, which demonstrated an effective compensation in its τ_f value and a lower dielectric loss. The microwave dielectric properties were discussed based upon the obtained densification, X-ray diffraction patterns and the microstructures of the ceramics. The correlation between the microstructures and the $Q \times f$ value was also investigated.

2. Experimental procedure

Samples of $(Mg_{0.95}Ni_{0.05})TiO_3$ and $CaTiO_3$ were individually synthesized by conventional solid-state methods from high-purity oxide powders (>99.9%): MgO,

* 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
doi:10.1016/j.jallcom.2008.04.099

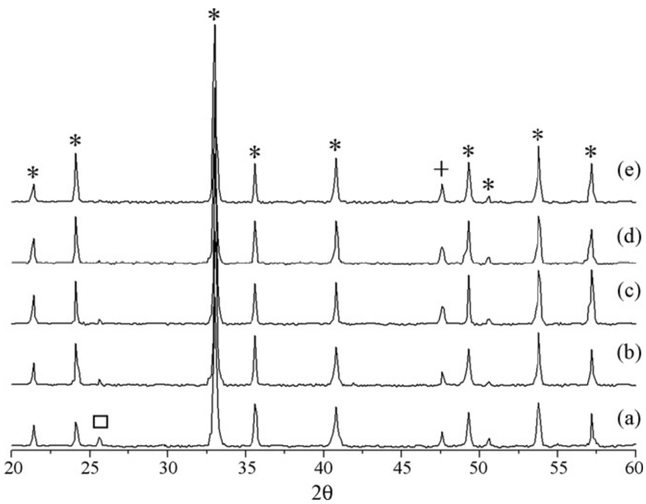


Fig. 1. X-ray diffraction patterns of $(1-x)(Mg_{0.95}Ni_{0.05})TiO_3$–$x$$CaTiO_3$ ceramics as a function of the x value, sintered at 1300 °C/4 h, (a) x = 0.02, (b) x = 0.04, (c) x = 0.06, (d) x = 0.08 and (e) x = 0.1. (*) Ilmenite, (+) perovskite, (□) $(Mg_{0.95}Ni_{0.05})Ti_2O_5$.

NiO, $CaCO_3$, and TiO_2. The starting materials were mixed according to the stoichiometry: $(Mg_{0.9}Ni_{0.05})TiO_3$ and $CaTiO_3$. They were then ground in distilled water for 24 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 to the desired composition $(1-x)(Mg_{0.95}Ni_{0.05})$–$x$$CaTiO_3$ and ground into a fine powder for 24 h. The fine powder together with the organic binder were forced through a 100-mesh sieve and pressed into pellets of 11 mm in diameter and 5 mm in thickness. These pellets were

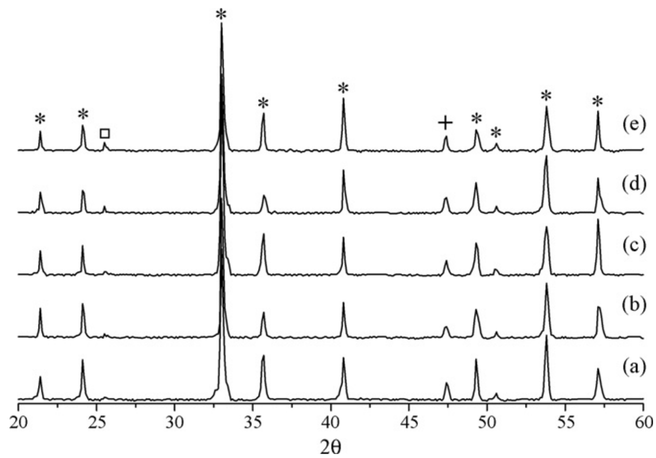


Fig. 2. X-ray diffraction patterns of $0.94(Mg_{0.95}Ni_{0.05})TiO_3$–$0.06CaTiO_3$ ceramics sintered at (a) 1250 °C, (b) 1275 °C, (c) 1300 °C, (d) 1325 °C, and (e) 1350 °C for 4 h.

sintered at temperatures of 1250–1350 °C for 4 h in air. Both the heating rate and the cooling rate were set at 10 °C/min.

The densities of the sintered ceramics were measured using the Archimedes method. The crystalline phases were analyzed using the X-ray powder diffraction method with Cu Kα radiation from 20° to 60° in 2θ. The scanning rate was 4° min^{-1}. The microstructure was observed with a scanning electron microscope (SEM). The dielectric constants and the unloaded Q values were measured using the Hakki–Coleman dielectric resonator method as modified and improved by Kobayashi–Katoh [7,8]. The apparatus consisted of parallel conducting brass plates and coaxial probes connected to an HP8757B network analyzer and an HP8350B sweep oscillator. The same technique was applied to measure the temperature coef-

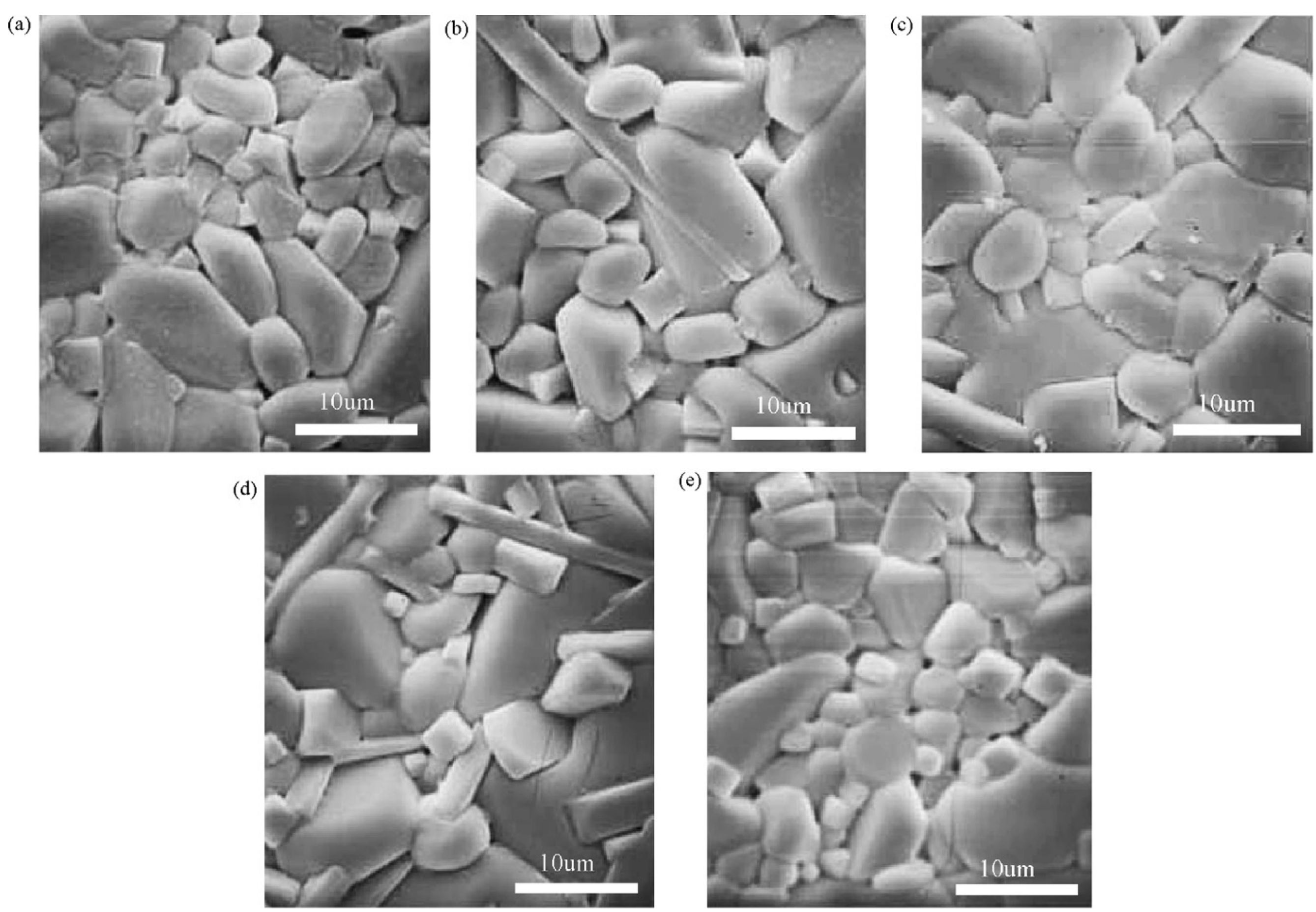


Fig. 3. SEM micrographs of $(1-x)(Mg_{0.95}Ni_{0.05})TiO_3$–$x$$CaTiO_3$ ceramics sintered at 1300 °C/4 h, (a) x = 0.02, (b) x = 0.04, (c) x = 0.06, (d) x = 0.08 and (e) x = 0.1.

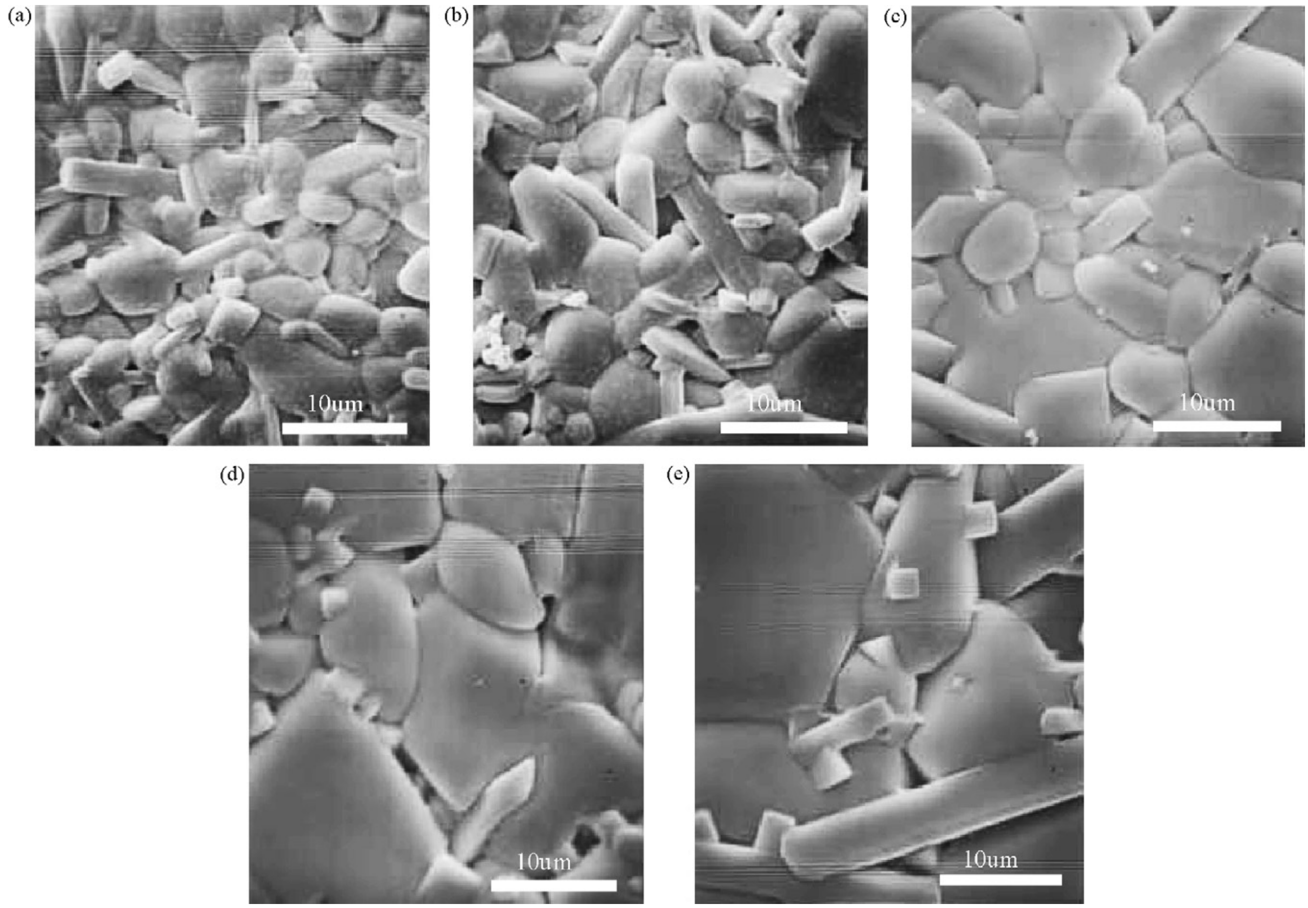


Fig. 4. SEM micrographs of $0.94(Mg_{0.95}Ni_{0.05})TiO_3$–$0.06CaTiO_3$ ceramics sintered at (a) 1250 °C, (b) 1275 °C, (c) 1300 °C, (d) 1325 °C and (e) 1350 °C for 4 h.

ficient of resonant frequency (τ_f). The test set was placed over a thermostat with a temperature range from 25 °C to 80 °C. The τ_f value (ppm/°C) was 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.

3. Results and discussion

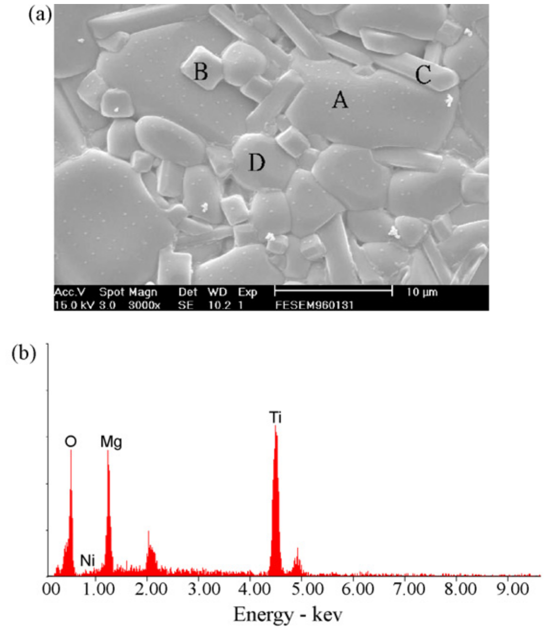
3.1. Phases and microstructures

The X-ray diffraction patterns of the $(1-x)(Mg_{0.95}Ni_{0.05})TiO_3$–$xCaTiO_3$ (hereafter referred to as MNCT) ceramic system sintered at 1300 °C/4 h with x ranging from 0.02 to 0.1 are shown in Fig. 1. MNCT ceramics showed a mixture of a main phase $(Mg_{0.95}Ni_{0.05})TiO_3$ and a minor phase $CaTiO_3$. The formation of MNT (ilmenite) and CT (perovskite) was due to the structure and ionic size differences between Ca^{2+} (1.00 Å) and Mg^{2+} (0.46 Å) [9]. Moreover, a second phase $(Mg_{0.95}Ni_{0.05})Ti_2O_5$ ($\varepsilon_r \sim 13.1$, $Q \times f$ ~30,000 GHz, $\tau_f \sim -43$ ppm/°C at 1300 °C) was also detected, which would lead to a degradation in the dielectric properties. It was attributed to that $MgTi_2O_5$ is usually formed as an intermediate phase and is difficult to completely eliminate from the sample prepared by mixed oxide route when MgO and TiO_2 reacts in a 1:1 molar ratio [10,11]. The intensity of the second phase decreased with increasing x owing to a decrease in the compositional content (Mg, Ni and Ti). Similar XRD patterns were obtained for specimen at different temperatures (Fig. 2) except that second phase $(Mg_{0.95}Ni_{0.05})Ti_2O_5$ was enhanced at higher temperatures. It showed an increase in its intensity as the sintering temperature increased.

The SEM micrographs of MNCT ceramics sintered at 1300 °C/4 h are demonstrated in Fig. 3. Significant change was not observed for grain size at different x values due to a small compositional variation (x = 0.02–0.1). Fig. 4 shows the SEM micrographs of MNCT ceramics with x = 0.06 at different temperatures. As the sintering temperature increased from 1250 °C to 1350 °C, the grain size increased. Rapid grain growth was observed for specimens at sintering temperatures above 1300 °C, resulting in a porous microstructure, which would certainly affect their microwave dielectric properties.

Fig. 5 shows the EDS results of $0.94(Mg_{0.95}Ni_{0.05})TiO_3$–$0.06CaTiO_3$ (94MNCT hereafter) ceramics sintered at 1300 °C for 4 h. Spot A (larger circular grain) shows that Mg and Ti were rich but Ca was almost free, while spot B (small square grain) reveals that Ca and Ti were rich but Mg was almost free. Spot C (needle shape grains) is the second phase of $MgTi_2O_5$ (Mg:Ti = 1:2), which causes the degradation in dielectric properties. Extra analysis of spot D (smaller circular grain) demonstrated the same composition as that of spot A. These results agreed well with those from Fig. 1.

The apparent densities of the MNCT system as a function of sintering temperature are shown in Fig. 6. With increasing sintering temperature, the density of the specimen increased to a maximum at 1300 °C and decreased thereafter. This increase in



(c)

	Atom(%)				
Spot	MgK	NiK	CaK	TiK	OK
A	19.61	1.57	0	23.68	55.15
B	0	0	24.65	26.75	48.6
C	13.4	0.74	0	25.84	60.02
D	21.92	2.04	0	22.93	55.38

Fig. 5. The EDS results of $0.94(Mg_{0.95}Ni_{0.05})TiO_3$–$0.06CaTiO_3$ ceramics sintered at 1300 °C for 4 h; (a) corresponding SEM micrograph (b) typical EDS and (c) obtained compositional ratio.

the bulk density is attributed to the grain growth resulted in a dense microstructure, as shown in Fig. 4. The decrease in the density, however, was mainly caused by the porous microstructure resulted from a rapid grain growth. Moreover, the density was also related to the compositions, and increased with increasing x since $CaTiO_3$ (D ~4.1 g/cm^3) possesses a higher density than that of $(Mg_{0.95}Ni_{0.05}Ti)O_3$ (D ~3.45 g/cm^3). At 1300 °C, the density of the MNCT ceramics increased from 3.18 g/cm^3 to 3.3 g/cm^3 as the x value increased from 0.02 to 0.08.

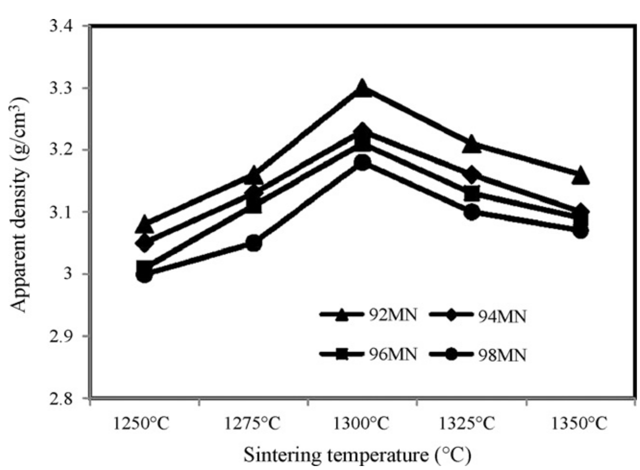


Fig. 6. Apparent density of $(1-x)(Mg_{0.95}Ni_{0.05})TiO_3$–$xCaTiO_3$ ceramics with different x values as a function of sintering temperature.

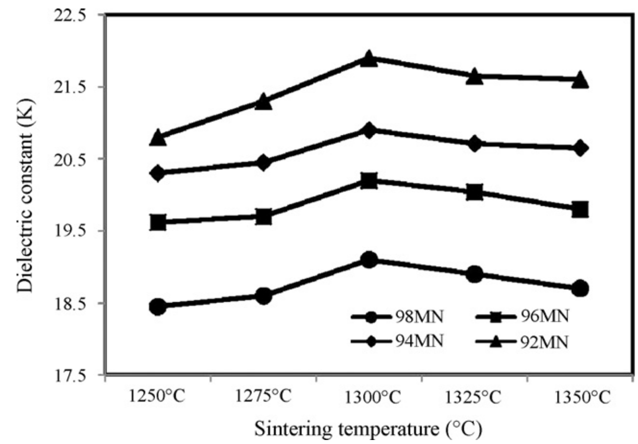


Fig. 7. Dielectric constant (ε_r) of $(1-x)(Mg_{0.95}Ni_{0.05})TiO_3$–$xCaTiO_3$ ceramics with different x values as a function of sintering temperature.

3.2. Microwave properties

Fig. 7 plots the dielectric constant of MNCT system as a function of sintering temperature. The dielectric constant increased with increasing sintering temperature to a maximum value at 1300 °C, and thereafter it decreased. The variation of ε_r value was mainly consistent with that of density. Moreover, the dielectric constant was also a function of the compositions and increased with increasing $CaTiO_3$ content since $CaTiO_3$ possesses a much higher dielectric constant than that of $(Mg_{0.95}Ni_{0.05})TiO_3$ ($\varepsilon_r \sim 170$ for $CaTiO_3$; ~17.2 for $(Mg_{0.95}Ni_{0.05})TiO_3$). At 1300 °C, the ε_r value of MNCT ceramics increased from 19.1 to 23.1 with as x increased from 0.02 to 0.08.

Fig. 8 shows $Q \times f$ value of MNCT system as a function of sintering temperature. The $Q \times f$ value is an important index for dielectric ceramics at microwave frequency since a higher $Q \times f$ value corresponding to a lower dielectric loss. The microwave dielectric loss is mainly not only determined by the density but also by the lattice vibrational modes, the pores, and the second phases [12]. The quality factor of $(Mg_{0.95}Ni_{0.05})TiO_3$ ($Q \times f$ value ~180,000 GHz) is much higher than that of $CaTiO_3$ ($Q \times f$ value ~3600 GHz) and hence it is expected that the $Q \times f$ values will decrease as the amount of $CaTiO_3$ increases from 0.02 to 0.08. The $Q \times f$ value increases when the sintering temperature increases from 1250 °C to 1300 °C. After reaching its maximum value at 1300 °C, the $Q \times f$ value decreased. The increase in $Q \times f$ value at low temperatures is due to the increase in density as well as the uniform morphology, as shown

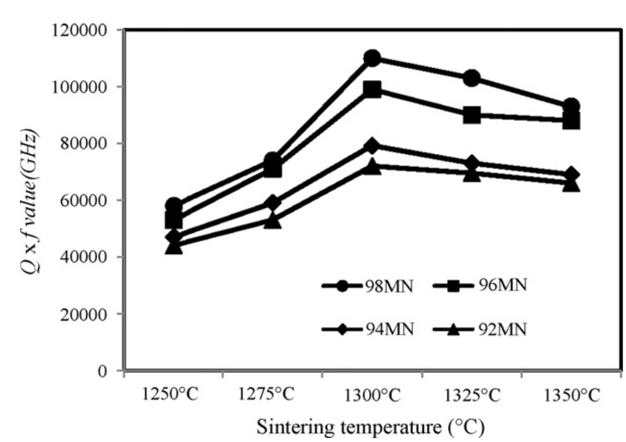


Fig. 8. $Q \times f$ value of $(1-x)(Mg_{0.95}Ni_{0.05})TiO_3$–$xCaTiO_3$ ceramics with different x values as a function of sintering temperature.

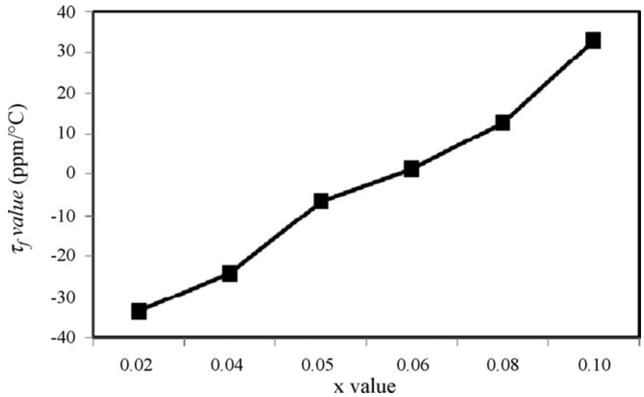


Fig. 9. τ_f value of $(1-x)(Mg_{0.95}Ni_{0.05})TiO_3$–$xCaTiO_3$ ceramics sintering at 1300 °C/4 h as a function of the x value.

in Figs. 4 and 6. At 1300 °C, a maximum $Q \times f$ value of 79,200 GHz (at 8 GHz) was obtained for the $0.94(Mg_{0.95}Ni_{0.05})TiO_3$–$0.06CaTiO_3$ ceramics. The degradation of $Q \times f$ value can be attributed to inhomogeneous grain growth which results in a reduction in its density. As a conclusion, the variation of $Q \times f$ is consistent with that of density, suggesting that dielectric loss of MNCT ceramics is mainly controlled by its bulk density.

The temperature coefficients of resonant frequency (τ_f) of MNCT ceramics sintered at 1300 °C/4 h as a function of x is shown in Fig. 9. The temperature coefficient of resonant frequency is related to the composition, the additives, and the second phase of the material. Due to the large positive τ_f value of $CaTiO_3$ (τ_f = 800 ppm/°C), the temperature coefficient of resonant frequency of MNCT ceramics rapidly increases with increasing x value. The τ_f value is shifted from negative to positive as the x value increases from 0.02 to 0.1. This implies that $\tau_f = 0$ can be obtained by adjusting the amount of the $CaTiO_3$ additive.

4. Conclusion

Microwave dielectric properties of $(1-x)(Mg_{0.95}Ni_{0.05})TiO_3$–$xCaTiO_3$ ceramics were investigated. For $(1-x)(Mg_{0.95}Ni_{0.05})TiO_3$–$xCaTiO_3$ ceramics sintered at 1250–1350 °C for 4 h, as the amount of $CaTiO_3$ (x value) increased from 0.02 to 0.1, the dielectric constant increased from 19.1 to 23.4, the temperature coefficient of resonant frequency (τ_f) increased from −33.5 ppm/°C to +33 ppm/°C, and the $Q \times f$ value decreased from 110,000 (at 8 GHz) to 72,000 (at 8 GHz). At the composition of $x = 0.06$, the $0.94(Mg_{0.95}Ni_{0.05})TiO_3$–$0.06CaTiO_3$ ceramics sintered at 1300 °C/4 h have excellent microwave dielectric properties: a dielectric constant ε_r of 20.9, a $Q \times f$ value of 79,200 (at 8 GHz), and a τ_f value of 1.2 ppm/°C.

Acknowledgement

This work was supported by the National Science Council of Taiwan under grant NSC 96-2221-E-006-117.

References

[1] C.L. Huang, J.J. Wang, Y.P. Chang, J. Am. Ceram. Soc. 90 (2007) 858.
[2] A. Yokoi, H. Ogawa, A. Kan, J. Euro. Ceram. Soc. 26 (2006) 2069.
[3] C.H. Hsu, C.F. Shih, C.C. Yu, H.H. Tung, M.H. Chung, J. Alloy Compd 461 (2008) 355–359.
[4] H. Su, S. Wu, Mater. Lett. 59 (2005) 2337.
[5] K. Wakino, Ferroelectric 91 (1989) 69.
[6] 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.
[7] B.W. Hakki, P.D. Coleman, IEEE Trans. Microwave Theor. Tech. 8 (1960) 402.
[8] Y. Kobayashi, M. Katoh, IEEE Trans. Microwave Theor. Tech. 33 (1985) 586.
[9] R.D. Shannon, C.D. Prewitt, Acta Crystallogr. B25 (1969) 925.
[10] C.L. Huang, C.L. Pan, Jpn. J. Appl. Phys. 41 (2002) 707.
[11] J. Liao, M. Senna, Mater. Res. Bull. 30 (1995) 385.
[12] B.D. Silverman, Phys. Rev. 125 (1962) 1921.