Journal of Alloys and Compounds 489 (2010) 541–544

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

$x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$(1-x)(La_{0.5}Na_{0.5})TiO_3$ ceramic at microwave frequency with a near zero temperature coefficient of resonant frequency

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ARTICLE INFO

Article history:
Received 26 August 2009
Received in revised form
16 September 2009
Accepted 17 September 2009
Available online 25 September 2009

Keywords:
Microwave dielectric
Oxides
X-ray diffraction
Dielectric properties

ABSTRACT

Dielectric properties of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$(1-x)(La_{0.5}Na_{0.5})TiO_3$ ceramic were investigated at microwave frequencies. A nearly 0 ppm/°C temperature coefficient of resonant frequency was realized at $x = 0.9$. A two-phase system was confirmed by XRD analysis. A dielectric material applicable to microwave devices with a $Q \times f$ of 20,000–87,000 GHz and a dielectric constant of 21.27–26.2 was obtained at 1100 °C after 4 h of sintering. The microwave dielectric material $0.9(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$0.1(La_{0.5}Na_{0.5})TiO_3$ sintered at 1150 °C for 4 h has a dielectric constant of 24.56, a $Q \times f$ of 68,000 GHz, and a τ_f value of 0 ppm/°C. It is proposed as a candidate dielectric for GPS patch antennas.

1. Introduction

High frequency passive components such as microwave dielectric resonators and antennas have been rapidly developed for cellular phones and global positioning systems [1,2]. Advantages of using dielectric ceramic materials include a potential size reduction of the microwave components and improved performance. In order to miniaturize the dimensions of devices and for the system to work with high efficiency and stability, dielectric materials for microwave resonators must have a combination 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). 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 must be precisely controlled.

$MgTiO_3$-$CaTiO_3$ ceramic is well known as a material for temperature-compensating-type capacitors, dielectric resonators, and patch antennas. It is made of a mixture of modified α-Al_2O_3 structured magnesium titanate ($MgTiO_3$: $\varepsilon_r \sim 17$, $Q \times f$ value ~160,000 at 7 GHz, and a zero τ_f) [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]. $0.95MgTiO_3$-$0.05CaTiO_3$ [5] ceramic has an $\varepsilon_r = 21$, $Q \times f = 56{,}000$ GHz, TCF = 0 ppm/°C, and a sintering temperature as high as of 1400 °C. For practical applications, the sintering temperature must be reduced. The $(Mg_xZn_{1-x})TiO_3$ system sintering temperature can be reduced to below 1000 °C, but there are limits to the $Q \times f$ value for the compositions with near zero TCF.

Cha et al. [6] showed that Co substitution improves the densification and $Q \times f$ value of $(Mg_{0.7}Zn_{0.3})TiO_3$. With the partial replacement of $(Mg_{0.7}Zn_{0.3})$ by Co, $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramic with an ilmenite-type structure sintered at a low sintering temperature of 1200 °C for 4 h was reported to have excellent dielectric properties with an ε_r value ~20, a $Q \times f$ value ~163,000 GHz at 10 GHz and a negative τ_f value ~−65 ppm/°C. Compounds with positive τ_f, such as cubic perovskite $(La_{0.5}Na_{0.5})TiO_3$ ceramic (ICDD #39-0065) has a dielectric constant ε_r value ~122, a $Q \times f$ value ~9800 at 3 GHz and a large positive τ_f value ~+480 ppm/°C. Therefore, compensation for the temperature coefficient of resonant frequency τ_f value can be made by employing z mixture of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ and $(La_{0.5}Na_{0.5})TiO_3$ ceramics. In this study, the microwave dielectric properties of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$(1-x)(La_{0.5}Na_{0.5})TiO_3$ ceramic were investigated. In addition, X-ray diffraction (XRD) pattering and scanning electron microscopy (SEM) analysis were employed to study the crystal structures and microstructures of the ceramics.

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0925-8388/$ – see front matter
doi:10.1016/j.jallcom.2009.09.103

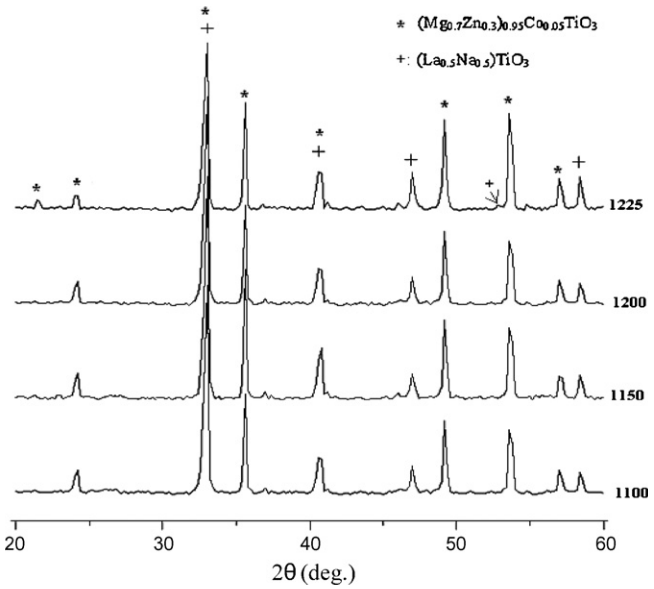

Fig. 1. X-ray diffraction patterns of $0.9(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$0.1(Na_{0.5}La_{0.5})TiO_3$ ceramics sintered at: (a) 1100 °C (b) 1150 °C, (c) 1200 °C, (d) 1225 °C for 4 h (*: $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$; +: $(La_{0.5}Na_{0.5})TiO_3$).

2. Experimental procedure

Samples of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$(1-x)(La_{0.5}Na_{0.5})TiO_3$ were prepared using the conventional solid state method. The starting materials were mixed according to a stoichiometric ratio. High purity oxide powders (>99.9%) La_2O_3, Na_2CO_3, MgO, TiO_2, CoO_2, and ZnO were weighed and mixed for 24 h with distilled water. The powders were weighted according to the composition $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ and $(La_{0.5}Na_{0.5})TiO_3$, and then milled with ZrO_2 balls for 12 h in distilled water and dried. The dried powders were calcined at 900 °C for 4 h, mixed according to the molar fraction $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$(1-x)(La_{0.5}Na_{0.5})TiO_3$ and the remilled for 12 h. A fine powder with 3 wt% of a 10% solution of polyvinyl alcohol (PVA) was used as a binder. Pellets with 11 mm in diameter and 5 mm in thickness were pressed using uniaxial pressing. A pressing pressure of 2000 kg/cm^2 was used for all samples. After debinding, the pellets were sintered at temperatures of 1100 °C–1125 °C for 4 h in air.

The crystalline phases of the calcined powder and the sintered ceramics were identified using X-ray diffraction pattern analysis. The microstructure observations and analysis of sintered surface were performed using a scanning electron microscope (SEM, Philips XL-40FEG). Energy dispersive spectroscopy (EDS) was used to identify the existence of second phases. The bulk densities of the sintered pellets were measured using the Archimedes method. The dielectric constant (ε_r) and the quality factor values (Q) at microwave frequencies were measured using the Hakki–Coleman [7] dielectric resonator method under TE_{011} and $TE_{01\sigma}$ modes as modified and improved by Courtney [8]. The dielectric resonator was positioned between two brass plates. A system combined with an HP8757D network analyzer and an HP8350B sweep oscillator was employed in the measurement. The same 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 of +25 °C to +80 °C. The τ_f value (ppm/°C) was calculated by noting the change in resonant frequency (Δf).

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

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

3. Results and discussion

X-ray diffraction patterns of $0.9(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$0.1(La_{0.5}Na_{0.5})TiO_3$ ceramic sintered at various temperatures for 4 h are shown in Fig. 1. $0.9(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$0.1(La_{0.5}Na_{0.5})TiO_3$ ceramic showed mixed phases of $0.9(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ as the main phase with $(La_{0.5}Na_{0.5})TiO_3$ as the minor phases. The crystal structures of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ and $(La_{0.5}Na_{0.5})TiO_3$ are trigonal (ICDD-PDF #00-006-0494) and cubic (ICDD-PDF #01-084-0443), respectively. The formation of mixed phases in the $0.9(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$0.1(La_{0.5}Na_{0.5})TiO_3$ ceramic system was due to structured differences. Therefore, a solid solution system could not be obtained. The XRD patterns of the $0.9(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$0.1(La_{0.5}Na_{0.5})TiO_3$ ceramic system did not significantly change with sintering temperature in the range of 1100–1225 °C.

Table 1
The EDX data of the $0.9(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$0.1(La_{0.5}Na_{0.5})TiO_3$ ceramics for Spots A and B.

Spots	Atom (%)						
	Mg–K	Co–K	Na–K	La–L	Ti–K	O–K	Zn–L
A	14.5	1.1	0	0	21.2	53.1	5.1
B	0	0	12.9	13.2	25.7	45.2	0

SEM photographs of $0.9(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$0.1(La_{0.5}Na_{0.5})TiO_3$ ceramics sintered at various temperatures for 4 h are shown in Fig. 2. The grain increase with increasing sintering temperatures obvious and the $0.9(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$0.1(La_{0.5}Na_{0.5})TiO_3$ ceramic system was not dense and the grain did not grow at 1100 °C. Porous microstructures were observed at 1100 °C. However, rapid grain growth was observed at 1200 °C and the pores were almost eliminated for the specimen sintered at 1150 °C. In the past report, Huang et al. [9], the EDX analysis exhibited several types of grains: large grains were identified as $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ and small cubic-shape grains were identified as $(La_{0.5}Na_{0.5})TiO_3$.

Energy dispersive X-ray (EDX) analysis was used in combination with scanning electron microscopy to distinguish each grain of $0.9(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$0.1(La_{0.5}Na_{0.5})TiO_3$ ceramic sintered at 1200 °C. The SEM micrograph of the prepared sample is shown in Fig. 3 and the corresponding EDX data of Spots A and B are illustrated in Table 1. From the EDX analysis, the grain morphology of the $0.9(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$0.1(La_{0.5}Na_{0.5})TiO_3$ ceramics exhibited two types of grains: large grains (such as Spot A) were identified as $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$, small cubic-shape grains (such as Spot B) were $(Na_{0.5}La_{0.5})TiO_3$.

Fig. 4 shows the bulk densities of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$(1-x)(La_{0.5}Na_{0.5})TiO_3$ ceramic at different sintering temperatures for 4 h. The densities increased with increasing sintering temperature due to the enlarged grain size, as shown in Fig. 2. The increase in bulk density with increasing sintering temperature might be due to the decrease in the number of pores, as shown in Fig. 2, while the decrease in bulk density might be due to abnormal grain growth. The bulk density seemed to saturate at 1150 °C. A maximum density of 4 g/cm^3 was obtained for $0.85(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$0.15(La_{0.5}Na_{0.5})TiO_3$ ceramic sintered at 1150 °C for 4 h.

Fig. 5 shows the dielectric constants curves of the $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$(1-x)(La_{0.5}Na_{0.5})TiO_3$ ceramic system at various sintering temperatures for 4 h. The relationship between ε_r values and sintering temperature shows the same trend as that between density and sintering temperature since higher density means lower porosity. The dielectric constant slightly increased with increasing sintering temperature. The ε_r values of $0.9(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$0.1(La_{0.5}Na_{0.5})TiO_3$ ceramics increased from 23.9 to 24.6 when the sintering temperature was increased from 1100 to 1225 °C.

Microwave dielectric loss can be divided into intrinsic loss and extrinsic loss. Intrinsic losses are mainly caused by lattice vibration modes while extrinsic losses are dominated by second phases, oxygen vacancies, grain sizes and densification or porosity. Interfacial polarization is thought to play an important role in porous materials. The quality factor values ($Q \times f$) of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$(1-x)(La_{0.5}Na_{0.5})TiO_3$ ceramic at various sintering temperatures are shown in Fig. 6. With increasing sintering temperature, the $Q \times f$ value increased to a maximum value and then decreased. A maximum $Q \times f$ value

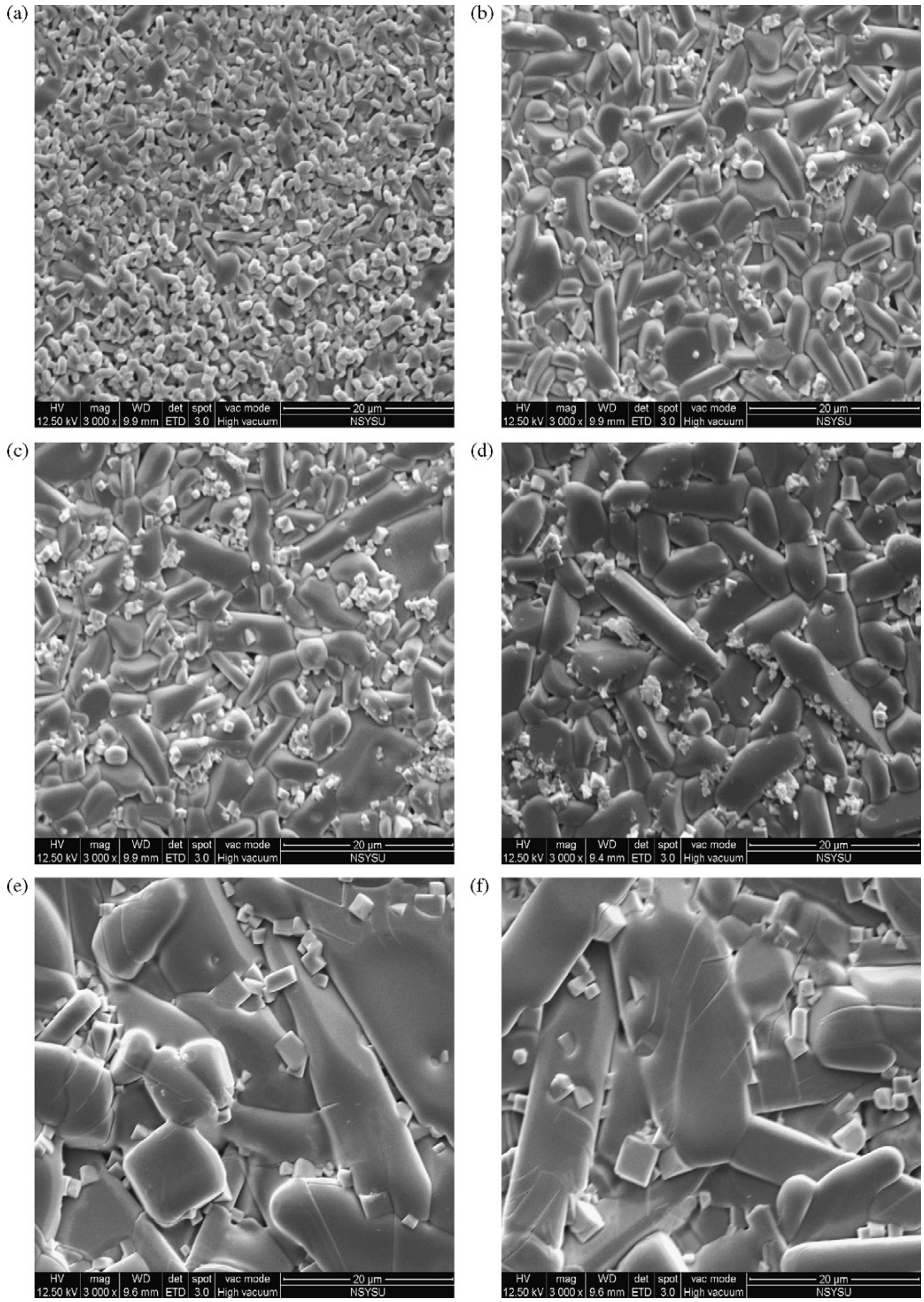

Fig. 2. SEM photographs of $0.9(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$0.1(La_{0.5}Na_{0.5})TiO_3$ ceramics sintered at different temperatures: (a) 1100 °C, (b) 1125 °C, (c) 1150 °C, (d) 1175 °C (e) 1200 °C (f) 1225 °C for 4 h.

of 87,000 GHz was obtained for $0.95(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$0.05(La_{0.5}Na_{0.5})TiO_3$ ceramic at 1150 °C. The degradation of the $Q \times f$ value can be attributed to abnormal grain growth at higher sintering temperatures, as shown in Fig. 2. The microwave dielectric loss is mainly caused by the lattice vibrational modes, pores, second phases, impurities, and lattice defects. Relative density also plays an important role in controlling dielectric loss, as has been shown for other microwave dielectric materials.

Fig. 7 shows the temperature coefficients of resonant frequency (τ_f) of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$(1-x)(La_{0.5}Na_{0.5})TiO_3$ ceramic at various sintering temperatures. In general, the temperature coefficient of resonant frequency (τ_f) is related to the composition and phases of the ceramics. The temperature coefficient of the resonant frequency (τ_f) was insensitive to the sintering temperature at all sintering temperature range. The τ_f values of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ and $(La_{0.5}Na_{0.5})TiO_3$ are −65 and +480 ppm/°C, respectively, so increasing the $(La_{0.5}Na_{0.5})TiO_3$ content makes the τ_f more positive. At $x = 0.9$, a near zero τ_f value of 0 ppm/°C was obtained. The developed microwave dielectric materials, $0.9(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$0.1(La_{0.5}Na_{0.5})TiO_3$ has a dielectric constant ε_r of 24.56, a $Q \times f$ value of ~68,000 GHz, and a τ_f value of 0 ppm/°C.

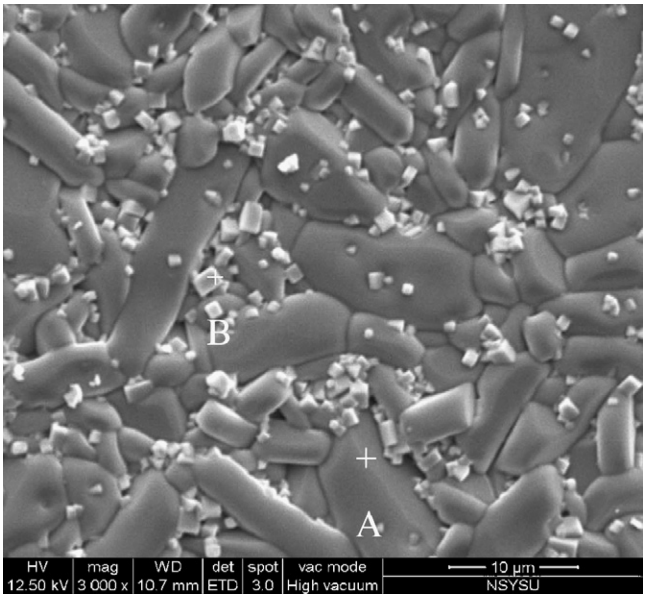

Fig. 3. The marks of SEM for $0.9(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$0.1(La_{0.5}Na_{0.5})TiO_3$.

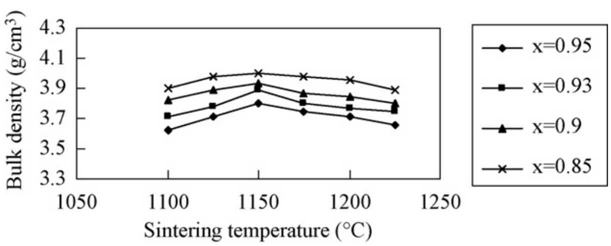

Fig. 4. Bulk density curves of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$(1-x)(La_{0.5}Na_{0.5})TiO_3$ ceramics at different sintering temperatures for 4 h.

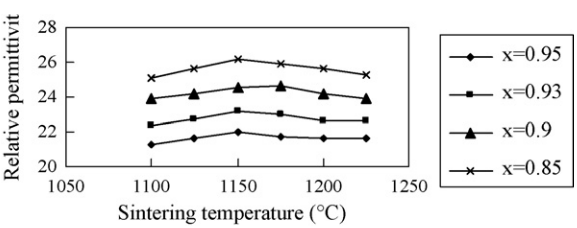

Fig. 5. Dielectric constants curves of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$(1-x)(La_{0.5}Na_{0.5})TiO_3$ ceramics at different sintering temperatures for 4 h.

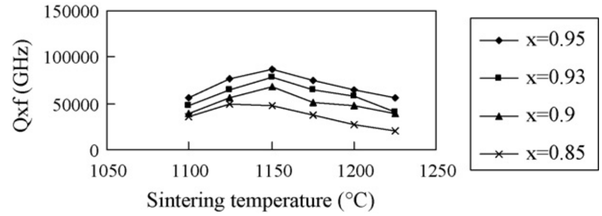

Fig. 6. $Q \times f$ values of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$(1-x)(La_{0.5}Na_{0.5})TiO_3$ system with different amount of CuO additives sintered at different temperatures for 4 h.

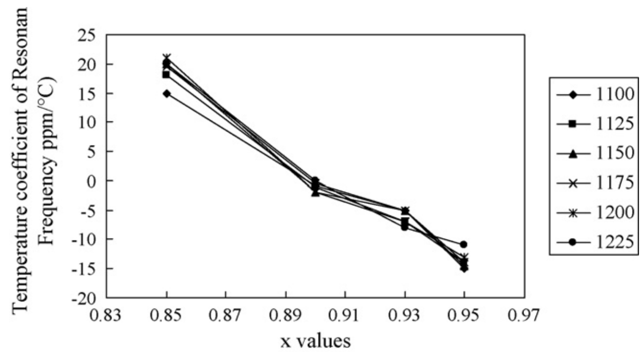

Fig. 7. τ_f values of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$(1-x)(La_{0.5}Na_{0.5})TiO_3$ system sintering at different temperatures for 4 h.

4. Conclusion

The dielectric properties of $x(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$(1-x)(La_{0.5}Na_{0.5})TiO_3$ ceramic were investigated. $0.9(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$0.1(La_{0.5}Na_{0.5})TiO_3$ ceramic exhibited mixed phases of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ as the main phase with some minor phases of $(La_{0.5}Na_{0.5})TiO_3$. For practical applications, a new microwave dielectric materials, $0.9(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$-$0.1(La_{0.5}Na_{0.5})TiO_3$ has been developed, exhibiting a dielectric constant ε_r of 24.56, a $Q \times f$ value of ~68,000 GHz, and a τ_f value of 0 ppm/°C.

References

[1] W. Werising, 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, Ferroelectrics 91 (1989) 69.
[4] R.C. Kell, A.C. Greenham, G.C.E. Olds, J. Am. Ceram. Soc. 56 (1973) 352.
[5] H. Ouchi, S. Kawashima, Jpn. J. Appl. Phys. 24 (1985) 60–64.
[6] H.J. Cha, D.H. Kang, Y.S. Cho, Mater. Res. Bull. 42 (2007) 265–273.
[7] B.W. Hakki, P.D. Coleman, IEEE Trans. Microwave Theory Tech. 8 (1960) 402.
[8] W.E. Courtney, IEEE Trans. Microwave Theory Tech. 18 (1970) 476.
[9] C.-L. Huang, G.-J. Li, J.-J. Wang, J. Alloys Compd. 472 (2009) 497–501.