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Characterization and dielectric behavior of V_2O_5-doped $0.9Mg_{0.95}Co_{0.05}TiO_3$–$0.1Ca_{0.6}La_{0.8/3}TiO_3$ ceramic system at microwave frequency

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ABSTRACT

The microwave dielectric properties and the microstructures of $Mg_{0.95}Co_{0.05}TiO_3$–$Ca_{0.6}La_{0.8/3}TiO_3$ ceramics, prepared by a mixed oxide route, have been investigated. With small amount of V_2O_5 additions, the sintering temperatures of $0.9Mg_{0.95}Co_{0.05}TiO_3$–$0.1Ca_{0.6}La_{0.8/3}TiO_3$ ceramics can be lowered to 1250 °C. The microwave dielectric properties are found strongly correlated with the sintering temperature as well as the amount of V_2O_5 additions. The $Q \times f$ value of $0.9Mg_{0.95}Co_{0.05}TiO_3$–$0.1Ca_{0.6}La_{0.8/3}TiO_3$ increased with increasing temperature to 1250 °C and decreased thereafter. The decrease in $Q \times f$ value was coincident with the abnormal grain growth. A maximum $Q \times f$ value of 58,000 (GHz) associated with a dielectric constant (ε_r) of 21.7 and a temperature coefficient (τ_f) of −10 ppm/°C, was achieved for 0.25 wt.% V_2O_5-doped samples at 1250 °C. Moreover, a cross-coupled compact hairpin filter with designed center frequency of 2.0 GHz is designed and fabricated using the proposed dielectric ceramic to study its performance. It also showed a substantial reduction in both insertion loss and size in comparison with other dielectrics FR4 and alumina.

1. Introduction

With the recent progress in the microwave communication system, microwave dielectric ceramics have become more important for the miniaturization of microwave device such as filters, duplexers voltage-controlled oscillators, and antennas. The advantage of using dielectric resonator is that it makes the size reduction of microwave components possible. Requirements for these dielectric devices must be combined with a high dielectric constant ($\varepsilon_r > 15$) for possible size miniaturization (size of a dielectric resonator is $.1/\sqrt{\varepsilon_r}$), a low dielectric loss ($Q > 5000$, where $Q = 1/\tan\delta$) for high frequency selectivity and low signal attenuation, and a near-zero temperature coefficient of resonant frequency (τ_f) for temperature stable circuits [1–5]. These three parameters are correlated to the size, frequency selectivity and temperature stability of the system, respectively. Several compounds such as (Zr, Sn)TiO_4, $Ba(Mg_{1/3}Ta_{1/3})O_3$, and (Mg, Ca)TiO_3 have been developed [6–14].

Magnesium titanate ($MgTiO_3$) ceramics is a popular dielectric material applied at microwave frequencies. With partial replacement of Mg^{2+} by Co^{2+}, the $Mg_{0.95}Co_{0.05}TiO_3$ ceramic with an ilmenite-type structure was reported to possess excellent dielectric properties with a dielectric constant (ε_r) of 16.8, a $Q \times f$ value of 230,000 (GHz) and a temperature coefficient (τ_f) of −54 ppm/°C [15]. However, it required sintering temperature as high as 1400–1450 °C.

There are three methods that commonly used for reducing the sintering temperature of dielectric ceramics: low-melting temperature glass addition, chemical processing, and the use of starting materials with small particle. The first method using liquid-phase glass sintering was found to effectively reduce the firing temperature. However, it also degraded the microwave dielectric properties of dielectric resonators. The chemical process often required a flexible procedure, which was expensive and time consuming. In the past, V_2O_5, Bi_2O_3, and a glass composition with a low melting point were used as flux formers [16,17]. It was also reported that tremendous temperature reduction can be achieved by adding CuO additives to the $BiNbO_4$ and $MgTiO_3$–$CaTiO_3$ systems [18,19].

The $(1-x)CaTiO_3$–$xLa_{2/3}TiO_3$ solid-solution system was first investigated by Kim et al. [20]. After sintering the specimens in air, they found that the solid-solution limit for the composition was $x = 0.96$. The superstructure reflection lines were detected for the composition $x = 0.8$. The microwave dielectric properties were also characterized at 10 GHz. The dielectric constant (ε_r) and the temperature coefficient (τ_f) decreased with an increase in the amount of La substited. The $Q \times f$ value increased rapidly at first, then increased steadily, and was almost linear for $x > 0.3$. The solid-solution limit of the composition $x = 0.96$ had the highest Q in the system and a high dielectric constant (ε_r) of 90. However, a poor

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temperature coefficient (τ_f) of +190 ppm/°C was obtained, which is not satisfactory for practical applications. Huang et al. reported that the $(1-y)CaTiO_3$–$yLa_{2/3}TiO_3$ solid-solution system exhibited excellent microwave dielectric properties when the y value was 0.4 [21]. Consequently, a $Ca_{0.6}La_{0.8/3}TiO_3$ ceramic with a high temperature coefficient of resonant frequency (τ_f) was utilized to adjust the τ_f value.

In our previous study, $Ca_{0.6}La_{0.8/3}TiO_3$ was added to $Mg_{0.95}Co_{0.05}TiO_3$ as a ceramic system of $(1-x)Mg_{0.95}Co_{0.05}TiO_3$–$xCa_{0.6}La_{0.8/3}TiO_3$ (hereafter referred to as MCT–CLT), which demonstrated an effective compensation in its temperature coefficient (τ_f) [2]. As $x=0.1$, the $0.9Mg_{0.95}Co_{0.05}TiO_3$–$0.1Ca_{0.6}La_{0.8/3}TiO_3$ (hereafter referred to as 91MCT–CLT) ceramic sintered at 1350 °C/4 h exhibited excellent microwave dielectric properties: a dielectric constant (ε_r) of 21.8, a $Q\times f$ value of 131,000 (GHz) and a temperature coefficient (τ_f) of −15.5 ppm/°C. In this study, V_2O_5 was added to the $(1-x)Mg_{0.95}Co_{0.05}TiO_3$–$xCa_{0.6}La_{0.8/3}TiO_3$ ceramics system as a sintered aid to lower its sintering temperature and to improve its microwave dielectric properties. The resultant microwave dielectric properties were analyzed based on the densification, X-ray diffraction patterns and microstructures of the ceramics (SEM and EDS). The correlation between the microstructures and the microwave dielectric properties was also investigated.

2. Experimental procedures

Samples of $Mg_{0.95}Co_{0.05}TiO_3$ and $Ca_{0.6}La_{0.8/3}TiO_3$ were individually synthesized by conventional solid-state methods from high-purity oxide powders (>99.9%): MgO, CoO, $CaCO_3$, La_2O_3 and TiO_2. The starting materials were mixed according to the stoichiometry: $Mg_{0.95}Co_{0.05}TiO_3$ and $Ca_{0.6}La_{0.8/3}TiO_3$ and ground in distilled water for 10 and 16 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 $(1-x)Mg_{0.95}Co_{0.05}$–$xCa_{0.6}La_{0.8/3}TiO_3$ with the additions of 0.25, 0.5, 0.75 and 1 wt.% of V_2O_5 as sintered aid and remilled for 24 h. The fine powder together with the organic binder were forced through a 100-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 1200–1300 °C for 4 h in air. The heating rate and the cooling rate were both set at 10 °C/min.

The powder and bulk X-ray diffraction (XRD, Rigaku D/Max III.V) spectra were collected using Cu Kα radiation (at 30 kV and 20 mA) and a graphite monochromator in the 2θ range of 20–60°. The microstructural observations and analysis of sintered surface were performed by a scanning electron microscopy (SEM, Philips XL-40FEG). The bulk densities of the sintered pellets were measured by the Archimedes method. The dielectric constant (ε_r) and the $Q\times f$ value at microwave frequencies were determined by using the Hakki–Coleman [22] dielectric resonator method as modified and improved by Courtney [23]. The disks were, in turn, placed between two parallel conductor plates. Then, the TE_{011} and TE_{012} modes were measured using a system combined with a HP8757D network analyzer and a HP8350B sweep oscillator. The dielectric constant was calculated from the resonant frequency of the TE_{011} mode of the cylindrical disk. For the Q_d measurement, the conductor loss resulting from the eddy currents around the conductive plate surfaces must be subtracted so as to obtain the dielectric quality factor. For this purpose, two disks with different height were prepared, one is for TE_{011} mode and the other is for TE_{012} mode, where the disk for the TE_{012} mode measurement has 2 times height as that of the disk for the TE_{011} mode. 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),

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

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

A cross-coupled compact hairpin filter with designed center frequency of 2.0 GHz is designed and measured through HP8757D network analyzer. In comparison with other dielectrics, filters were also fabricated on other substrate materials (such as FR4 and alumina).

3. Results and discussion

The XRD patterns of 0.25 wt.% V_2O_5-doped 91MCT–CLT ceramics at different sintering temperatures for 4 h are shown in Fig. 1. The crystal structure of $Mg_{0.95}Co_{0.05}TiO_3$ and $Ca_{0.6}La_{0.8/3}TiO_3$ are known to be the ilmenite type structure and pseudo-cubic perovskite crystal [15,20]. A significant change was not observed in XRD patterns of the 91MCT–CLT ceramics with 0.25 wt.% V_2O_5 sintered at 1200–1300 °C. Second phase $Mg_{0.95}Co_{0.05}Ti_2O_5$ usually formed as an intermediate phase during the growth, was identified and difficult to completely eliminate from the sample prepared by mixed oxide route [24]. The forming of the second phase $Mg_{0.95}Co_{0.05}Ti_2O_5$ was mainly due to the LOI of the starting powder MgO. It is also possibly a result from the following reaction:

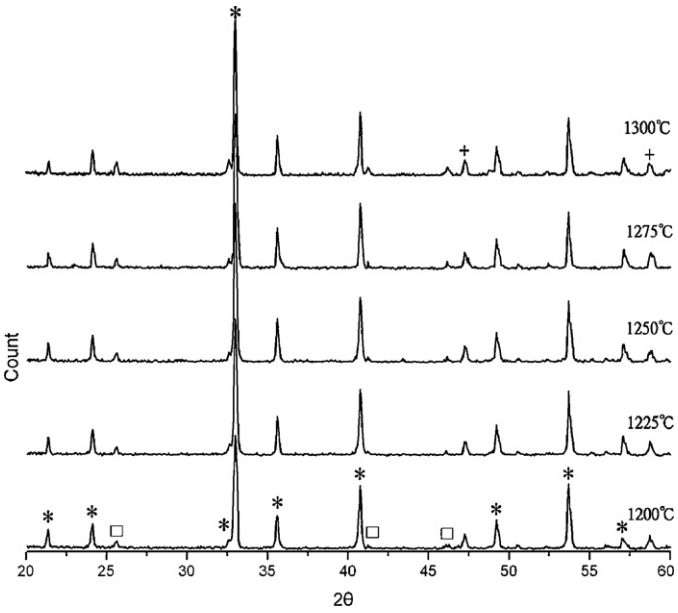

Fig. 1. X-ray diffraction patterns of 91MCT–CLT ceramic with 0.25 wt.% V_2O_5 additions at different sintering temperatures for 4 h (*: ilmenite, +: perovskite, □: $Mg_{0.95}Co_{0.05}Ti_2O_5$).

$$2Mg_{0.95}Co_{0.05}TiO_3 \rightarrow Mg_{0.95}Co_{0.05}Ti_2O_5 + Mg_{0.95}Co_{0.05}O \quad (2)$$

Moreover, the second phase $Mg_{0.95}Co_{0.05}Ti_2O_5$ was enhanced at higher V_2O_5 doping level. The formation of Second phase $Mg_{0.95}Co_{0.05}Ti_2O_5$ in the $Mg_{0.95}Co_{0.05}TiO_3$ ceramics would cause a serious drop in the quality factor of 91MCT–CLT ceramics [25]. Similar results of the X-ray diffraction pattern, however, were obtained for V_2O_5-doped specimens at 1250 °C comparison to pure 91MCT–CLT ceramics at 1250 °C are shown in Fig. 2.

The lattice parameters of 91MCT–CLT ceramics with different amount of V_2O_5 addition sintering at 1250 °C/4 h were also measured in this study as shown in Table 1. It was found that

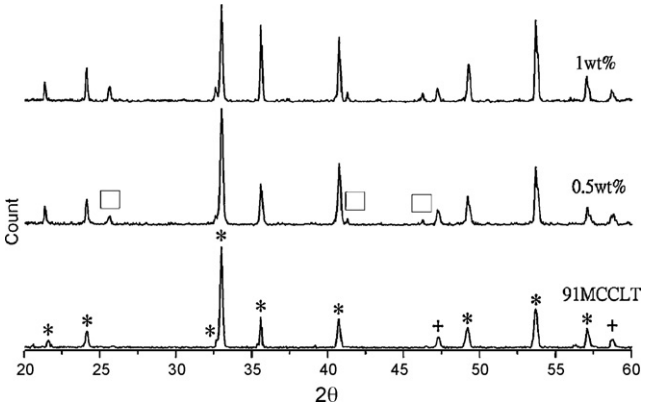

Fig. 2. X-ray diffraction patterns of 91MCT–CLT ceramic with various amount of V_2O_5 additions sintered at 1250 °C and pure 91MCT–CLT ceramic sintered at 1350 °C.

Table 1
The lattice parameter of 91MCT–CLT ceramic sintered at 1250 °C/4 h with different amount of V_2O_5 addition.

V_2O_5 additions	a (nm)	c (nm)
0 wt.%	0.5054	1.3899
0.25 wt.%	0.5066 ± 0.00072	1.39184 ± 0.00266
0.5 wt.%	0.5065 ± 0.00138	1.39145 ± 0.00511
0.75 wt.%	0.5058 ± 0.00026	1.3931 ± 0.00096
1.0 wt.%	0.505 ± 0.00055	1.3832 ± 0.00203

$MgTiO_3$ has a hexagonal structure with the following lattice parameters: $a = b = 0.5054$ nm, $c = 1.3898$ nm (ICDD-PDF#00-006-0494). The results illustrate that the replacement of Mg by 0.05 mol of Co leads to a variation in the lattice parameters. This is because the relatively small Co^{2+} ions (radii = 0.082 nm; Mg^{2+} ions radii = 0.078 nm) are added to $MgTiO_3$, making the lattice of $Mg_{0.95}Co_{0.05}TiO_3$ locally distorted. When $Ca_{0.6}La_{0.8/3}TiO_3$ was added to $Mg_{0.95}Co_{0.05}TiO_3$ to form a ceramic system of MCT–CLT, the lattice parameters of $Mg_{0.95}Co_{0.05}TiO_3$ did not change with $Ca_{0.6}La_{0.8/3}TiO_3$ content. Furthermore, the formation of mixed phases in the MCT–CLT ceramics system was due to structural differences and because the average ionic radii of Ca^{2+} (0.106 nm) and La^{3+} (0.122 nm) were larger than these of Mg^{2+} (0.078 nm) and Co^{2+} (radii = 0.082 nm). This confirms the existence of a two-phase ceramic system of MCT–CLT, with $Mg_{0.95}Co_{0.05}TiO_3$ as the main crystalline phase and $Ca_{0.6}La_{0.8/3}TiO_3$ as the minor phase. These results are in agreement with XRD patterns.

The SEM images of the 91MCT–CLT ceramics with 0.25 wt.% V_2O_5 additions at different sintering temperatures for 4 h are illustrated in Fig. 3. As shown in Fig. 3, the 91MCT–CLT ceramic with 0.25 wt.% V_2O_5 addition was not dense and the grains did not grow at 1200 °C. The grain size increased with the increasing of sintering temperature and the number of pores decreasing. However, over sintering (1275 and 1300 °C) would cause abnormal grain growth result in porous specimens as observed in the SEM photographs. That may directly affect the microwave dielectric properties of the 91MCT–CLT ceramics.

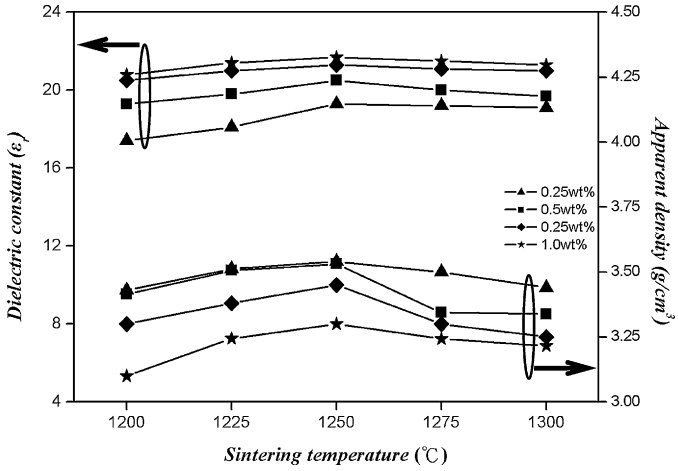

Fig. 4. Apparent density and dielectric constant (ε_r) of 91MCT–CLT ceramics with various V_2O_5 additions as functions of the sintering temperature.

Fig. 4 shows the bulk density and dielectric constant (ε_r) of 91MCT–CLT ceramics with different V_2O_5 additions after being sintered at various sintering temperatures for 4 h. The density increased with increasing sintering temperature because the ceramics became denser. With increasing the sintering temperature, the bulk density of the V_2O_5-doped 91MCT–CLT ceramics was found to increase to a maximum value at 1250 °C and thereafter

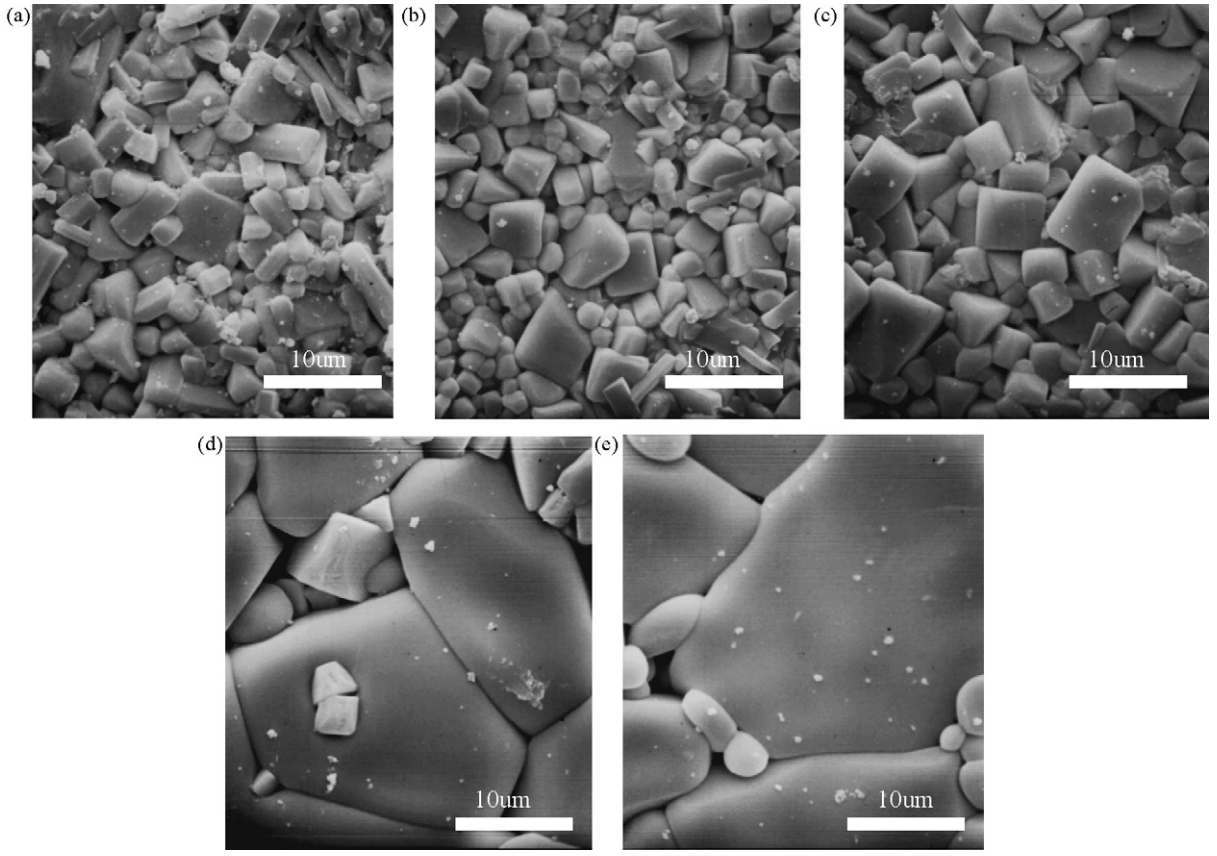

Fig. 3. SEM micrographs of 91MCT–CLT ceramic with 0.25% V_2O_5 additions sintered at (a) 1200 °C, (b) 1225 °C, (c) 1250 °C, (d) 1275 °C, and (e) 1300 °C for 4 h.

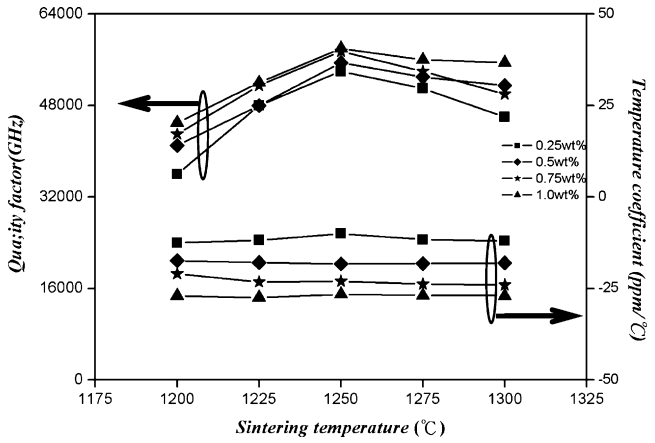

Fig. 5. Quality factor ($Q \times f$) and temperature coefficient (τ_f) of the 91MCT–CLT ceramics with various V_2O_5 additions as functions of the sintering temperature.

Table 2
Measure and calculated results of the Hairpin resonators for different substrates.

	Calculations	Measurements
FR4	f_o = 2.0 GHz	f_o = 2.0 GHz
	S_{11} = −21.5 dB	S_{11} = −26.19 dB
l_1 = 12.7 mm	S_{21} = −2.64 dB	S_{21} = −2.9 dB
l_2 = 24.5 mm	BW = 9%	BW = 85%
g = 0.50 mm	f_1 = 1.68 dB	f_1 = 1.685 dB
s = 0.40 mm	f_2 = 2.46 dB	f_2 = 2.46 dB
Al_2O_3	f_o = 1.975 GHz	f_o = 2.0 GHz
	S_{11} = −16.5 dB	S_{11} = −27.5 dB
l_1 = 11.95 mm	S_{21} = −1.19 dB	S_{21} = −0.93 dB
l_2 = 18.85 mm	BW = 10%	BW = 10%
g = 0.40 mm	f_1 = 1.70 dB	f_1 = 1.68 dB
s = 0.35 mm	f_2 = 2.51 dB	f_2 = 2.5 dB
91MCT–CLT	f_o = 1.985 GHz	f_o = 2.0 GHz
	S_{11} = −17.8 dB	S_{11} = −34.0 dB
l_1 = 8.58 mm	S_{21} = −0.87 dB	S_{21} = −0.75 dB
l_2 = 13.72 mm	BW = 10%	BW = 10%
g = 0.40 mm	f_1 = 1.69 dB	f_1 = 1.70 dB
s = 1.00 mm	f_2 = 2.39 dB	f_2 = 2.40 dB

decrease. The increase in bulk density with increasing sintering temperature might be due to the decrease in the number of pores as observed in Fig. 3. While the sintering temperature above 1250 °C, the decrease in bulk density might be due to abnormal grain growth. The relationships between dielectric constant (ε_r) and sintering temperatures revealed the same trend with those between densities and sintering temperatures since higher density means lower pores (ε_r = 1). The increase in the dielectric constant (ε_r) could be explained as owing to higher densities. The dielectric constant (ε_r) rapidly increased from 1200 to 1300 °C and saturated at 21–22 for the well-sintered ceramics.

Fig. 5 demonstrates the $Q \times f$ values and temperature coefficient of resonant frequency (τ_f) of the V_2O_5-doped 91MCT–CLT ceramics system are investigated as a function of sintering temperature. The $Q \times f$ values exhibits the same trend as that of density observed in Fig. 4. As the sintering temperature increase, the $Q \times f$ values reach a maximum value of 58,000 (GHz) at 1250 °C and then decrease with the further increase of sintering temperature. The degradation of $Q \times f$ value was attributed to abnormal grain growth as observed in Fig. 3. Since the V_2O_5 addition would enhance the densification of the specimen, individual maximum $Q \times f$ value appeared at lower sintering temperature for higher V_2O_5-doped 91MCT–CLT ceramics. 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 [26]. Relative density also plays an important role in controlling the dielectric loss, and has been shown for other microwave dielectric materials. The $Q \times f$ value of 91MCT–CLT ceramics decreased with increasing V_2O_5 addition, which was not consistent with the variation of density. Instead of the density, the decrease in $Q \times f$ value was due to the formation of second phase $Mg_{0.95}Co_{0.05}Ti_2O_5$ as well as the increase in V_2O_5 content as observed in Fig. 2. The temperature coefficient of resonant frequency (τ_f) is well known related to the composition and the second phase of a material. It was observed that the τ_f value shifted toward the negative direction with increasing V_2O_5 content. The τ_f value decreased almost linearly from −10 to −26.6 ppm/°C as V_2O_5 content increased from 0.25 to 1 wt.%. According to the XRD patterns, as shown in Fig. 2, the formation of second phase $Mg_{0.95}Co_{0.05}Ti_2O_5$ appeared with increasing of V_2O_5 content. It can be explained that pure 91MCT–CLT has a τ_f value of −15.5 ppm/°C while $Mg_{0.95}Co_{0.05}Ti_2O_5$ demonstrates the τ_f value of −38.9 ppm/°C. For practical applications, a modification in the temperature stability is necessary for MCT–CLT ceramics.

To put to the proof of performance of the proposed material of 91MCT–CLT ceramic with 0.25 wt.% V_2O_5-doped, a cross-coupled compact hairpin filter with designed center frequency of 2.0 GHz is designed and fabricated on different dielectric substrates: FR4 (ε_r = 4.7) alumina (ε_r = 9.7), and 91MCT–CLT ceramic with 0.25 wt.% V_2O_5-doped (ε_r = 21.7) [27–30]. Fig. 6 shows the physical layout of the designed filter with the central frequency of 2.0 GHz and the measurement results are illustrated in Table 2. In comparison with FR4 and alumina, the filter using 91MCT–CLT ceramic with 0.25 wt.% V_2O_5-doped not only shows a tremendous reduction in the insertion loss, but also demonstrates a marvelous cut in its efficacious dimensions.

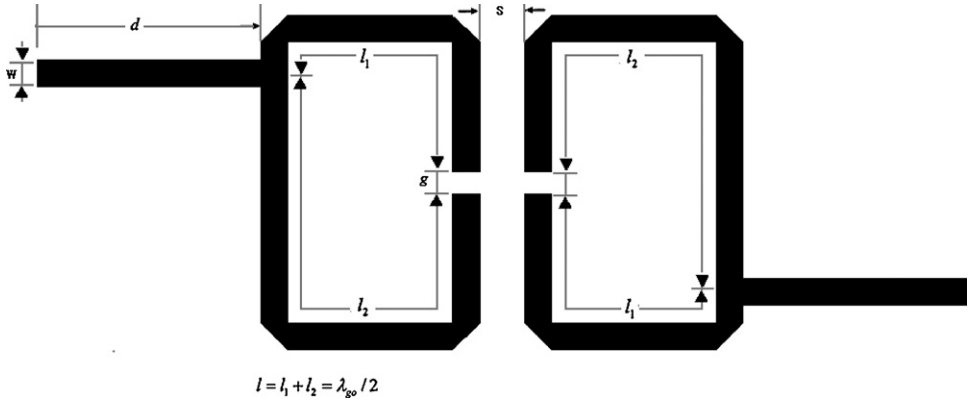

Fig. 6. Layout of the filter using two open-loop ring resonators with asymmetric tapping feed lines.

4. Conclusions

The effect of V_2O_5 addition on the microwave dielectric properties and the microstructures of $(1-x)Mg_{0.95}Co_{0.05}TiO_3$–$xCa_{0.6}La_{0.8/3}TiO_3$ ceramics were investigated. The sintering temperature of $0.9Mg_{0.95}Co_{0.05}TiO_3$–$0.1Ca_{0.6}La_{0.8/3}TiO_3$ ceramics with the V_2O_5 addition can be decreased about 100 °C. The dielectric constants of 91MCT–CLT ceramics decrease slightly and the temperature coefficients of 91MCT–CLT ceramics decrease with the increase amount of V_2O_5 addition. A maximum quality factor $Q \times f$ of 58,000 (GHz) associated with a dielectric constant (ε_r) of 21.7 and a temperature coefficient (τ_f) value of −10 ppm/°C, was achieved for 0.25 wt.% V_2O_5-doped samples at 1250 °C. In comparison with FR4 and alumina, the filter using 91MCT–CLT ceramic with 0.25 wt.% V_2O_5-doped not only shows a tremendous reduction in the insertion loss, but also demonstrates a marvelous cut (>40%) in its efficacious dimensions.

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