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Improved high Q value of $MgTiO_3$–$CaTiO_3$ microwave dielectric resonator using WO_3-doped at lower sintering temperature for microwave applications

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ABSTRACT

The effect of WO_3 additive on the microstructures, the phase formation and the microwave dielectric properties of $MgTiO_3$–$CaTiO_3$ ceramics system were investigated. The sintering temperature of WO_3-doped $0.95MgTiO_3$–$0.05CaTiO_3$ (95MCT) ceramics can be lowered to 1175 °C. The microwave dielectric properties are found strongly to correlate with the sintering temperature as well as the amount of WO_3 addition. At 1250 °C 95MCT ceramics with 0.5 wt% WO_3 addition gives a dielectric constant ε_r of 20.3, a $Q \times f$ value of 66,000 (GHz) and a τ_f value of −8.2 ppm/°C. A band-pass filter is designed and simulated using the proposed dielectric to study its performance.

1. Introduction

$MgTiO_3$-based ceramics is finding wide applications as dielectrics in resonators and filters for communication and radar systems operating at microwave frequencies. The development of microwave dielectric resonator for communication systems such as cellular phones and global positioning systems has been rapidly growing in the past decade [1,2]. The advantage of using dielectric resonators is that it makes the size reduction of microwave components possible. To achieve the requirements, these dielectric resonators must be combined with a high dielectric constant ($\varepsilon_r > 15$) for possible size miniaturization (size of a dielectric resonator $\sim 1/\sqrt{\varepsilon_r}$), 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 circuit. Magnesium titanate-based ceramics is one of the popular microwave dielectric materials, and has been widely applied in the coaxial type, large dimensional resonators and GPS antenna when operating at higher frequencies. Since most of the known commercial dielectric materials for high frequency applications have high sintering temperatures, they would certainly increase the manufacturing cost. Three methods are commonly used for reducing the sintering temperature of dielectric ceramics: low-melting glass addition, chemical processing, and using starting materials with smaller particle sizes. The method involving liquid-phase sintering was found to effectively lower the firing temperature. However, it also decreased the microwave dielectric microwave dielectric properties of ceramics. The chemical process often required a flexible process that increased the cost and time required to fabricate dielectric devices. Since tungsten-based dielectric materials are well-known low -sintering-temperature ceramics and have been widely investigated, WO_3 is chosen as a sintering aid in this study.

$MgTiO_3$–$CaTiO_3$ (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 magnesium titanate ($MgTiO_3$: ε_r ~17, $Q \times f$ value ~160,000 at 7 GHz and τ_f value ~−55 ppm/°C) [3] and calcium titanate ($CaTiO_3$: ε_r ~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 ε_r ~21, Q ~8000 at 7 GHz, and a zero τ_f value. However, it required sintering temperatures as high as 1400–1500 °C. Many researchers made efforts to study the microstructures and the microwave dielectric properties of the 95MCT ceramics by adding various additives or varying processing. Ferreira et al. [5,6] had serious reports of microwave dielectric properties of MCT ceramics. Doping with La_2O_3 and Cr_2O_3 enhanced the densification of MCT ceramics prepared by a mixed oxide route at 1400 °C. It increased the quality factor but decreased the dielectric constant. The τ_f value was not reported. MCT ceramics prepared by the chemical technique could be sintered at lower temperature, and gave excellent dielectric properties ($\varepsilon_r = 19.1$, $Q \times f = 8400$ at 8 GHz and τ_f unreported). However, the chemical process often required a flexible procedure that would increase the cost and time required to fabricate microwave dielectric components. The liquid phase sin-

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tering by adding glass or low melting point materials was found to effectively lower the firing temperature, as in our previous reports [7–10]. In this paper, WO_3 was added to $0.95MgTiO_3$–$0.05CaTiO_3$ ceramic system as a sintering aid to lower its sintering temperature. The resultant microwave dielectric properties were analyzed based upon the densification, the X-ray diffraction patterns and the microstructures of the ceramics. In addition, the low-temperature sintered microstructures of MCT ceramics were also correlated with its microwave dielectric properties. The correlation between the microstructure and the $Q \times f$ value was also investigated.

2. Experimental procedures

Samples of $MgTiO_3$ and $CaTiO_3$ were individually synthesized by conventional solid-state methods from high-purity oxide (>99.9%) powders: MgO, $CaCO_3$ and TiO_2. The starting materials were mixed according to the stoichometery of $MgTiO_3$ and $CaTiO_3$, and ground in distilled water for 10 h in a balling mill with agate balls. Both mixtures were dried and calcined at 1100 °C for 4 h. Impurities containing plastic steel would burn out during firing. The calcined powders were mixed as desired composition $0.95MgTiO_3$–$0.05CaTiO_3$ with different amounts of WO_3 additions as-sintering aids and re-milled for 5 h with PVA solution as a binder. The powders were sieved with dimension of 11 m in diameter and 5 mm in thickness. The pellets were sintered at temperatures of 1170–1350 °C for 4 h in air. The heating and cooling rates of the samples were 10 °C/min.

The microstructure observation of surfaces of the sintered ceramics was performed by scanning electron microscopy (SEM, JEOL JSM 6400, Japan). The crystalline phases of the sintered ceramics were identified using an X-ray diffraction (XRD, D5000 Diffractometer, Seimens, Germany) pattern. 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 and Coleman [11] dielectric resonator method as modified and improved by Courtney [12]. A system combining a HP8757D network analyzer and a HP8350B sweep oscillator was employed in the measurement. The disks were, in turn, placed between two parallel brass plates. The TE_{011} and TE_{012} modes were measured using a HP8510B network analyzer. The dielectric constant was calculated from the resonant frequency of the TE_{011} mode of the cylindrical disk. For the unloaded Q measurement, the conductor loss resulting from the eddy currents around the conductive plate surfaces must be subtracted to obtain the dielectric quality factor. For this purpose, two disks with different heights were prepared, one for the TE_{011} mode and the other is for the TE_{012} mode, where the disk for the TE_{012} mode measurement is twice the height of the disk for the TE_{011} mode. An 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 +20 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 represent the resonant frequencies at T_1 and T_2, respectively.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of as-sintered 95MCT ceramics with various amounts of WO_3 additions. MCT ceramics showed mixed phases of $MgTiO_3$ as the main phase associated with $CaTiO_3$ and $MgTi_2O_5$ as the minor phases. It is understood that the crystal of $MgTiO_3$ and $CaTiO_3$ are trigonal (JCPDS #06-0494) and orthorhombic (JCPDS #22-0153), respectively. $MgTi_2O_5$, usually formed as an intermediate phase, was identified and difficult to completely eliminate from the sample prepared by mixed oxide route. The formation of $CaTiO_3$ in MCT ceramics was due to the structure difference and the larger ionic size difference between Ca^{2+} (1.00 Å) and Mg^{2+} (0.64 Å). More amount of WO_3 addition seemed to inhibit the formation of $CaTiO_3$, but slightly enhance the formation of $MgTi_2O_5$ in MCT ceramics. Result of the X-ray diffraction pattern in Fig. 1, however, was obtained for WO_3-doped specimens at 1300 °C in comparison to that of pure 95MCT at 1300 °C. With 2 wt% WO_3 addition, both $CaTiO_3$ and $MgTi_2O_5$ phases were observed and stable at temperatures 1300 °C. Although a very small amount of $CaWO_4$ was identified, it became significant when the WO_3 addition was increased to 2 wt%. With WO_3 addition, the secondary phase of $CaWO_4$ was enhanced, and this which lower the $Q \times f$ value as we can see in Fig. 5.

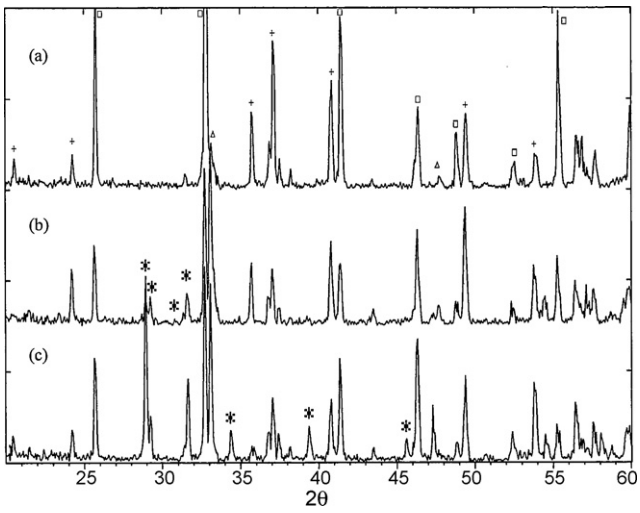

Fig. 1. X-ray diffraction patterns of $0.95MgTiO_3$–$0.05CaTiO_3$ ceramics sintered at 1300 °C with (a) 0.5 wt% (b) 2 wt% (c) 5 wt% WO_3 additions. (+) $MgTiO_3$, (Δ) $CaTiO_3$, (□) $MgTi_2O_5$, (*) $CaWO_4$).

The SEM photographs of 95MCT ceramics with 0.5 wt% WO_3 addition at different sintering temperatures for 4 h are illustrated in Fig. 2. The 95MCT ceramics was not dense and the grain did not grow at 1170 °C. However, rapid grain growth was observed at 1250 °C and the pores were almost eliminated for specimen sintered at 1300 °C due to the effect of liquid phase.

Fig. 3 shows the bulk densities of 95MCT ceramics with various amounts of WO_3 additions at different sintering temperature for 4 h. The densities increased with increasing sintering temperature due to enlarged grain size as observed in Fig. 2. They seemed to saturate at 1250 °C despite of the amount of WO_3 addition. A maximum density of 3.8 g/cm^3 was obtained for 95MCT ceramics with 5 wt% WO_3 1300 °C for 4 h. It implies that WO_3 addition can effectively lower the sintering temperature of 95MCT ceramics.

Fig. 4 shows the dielectric constants of 95MCT ceramics with different amount of WO_3 as functions of their sintering temperatures. 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. Moreover, higher WO_3 content also increased ε_r value could be explained as the result of higher density. The ε_r values of the 95MCT ceramics with 0.5 wt% WO_3 addition increased from 19.89 to 20.23 as the sintering temperature increased from 1170 to 1250 °C.

The quality factor values ($Q \times f$) of 95MCT ceramics with various WO_3 additions at different sintering temperatures are demonstrated in Fig. 5. 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 60,000 GHz was obtained for 95MCT ceramics with 0.5 wt% WO_3 addition at 1250 °C. The decrease of $Q \times f$ value was attributed to abnormal grain growth as observed in Fig. 2. Since the liquid phase would enhance the densification of the specimen, individual maximum $Q \times f$ value appeared at lower sintering temperature for higher WO_3-doped 95MCT. 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. The $Q \times f$ value of 95MCT ceramics decreased with increasing WO_3 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

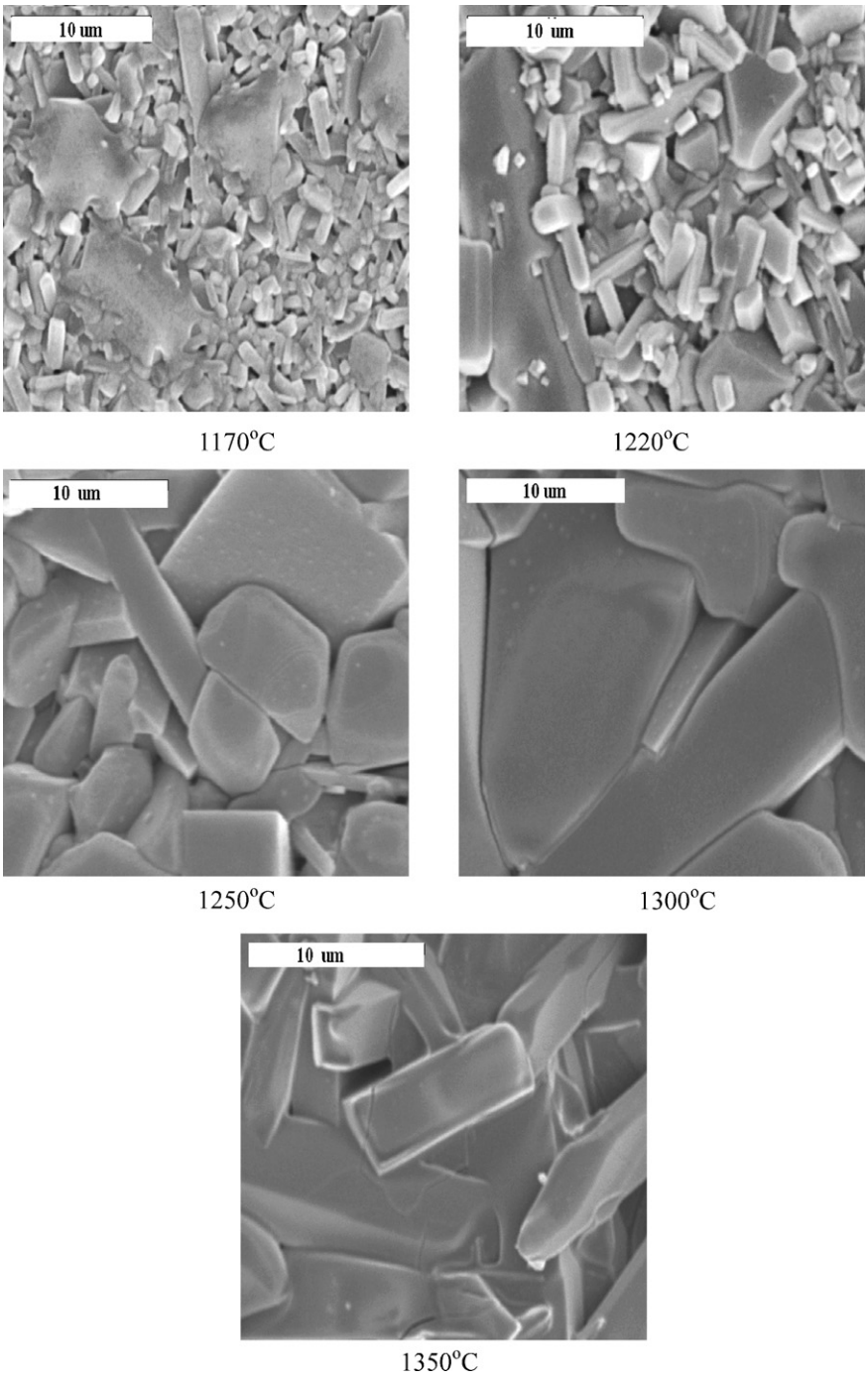

Fig. 2. SEM photographs of $0.95MgTiO_3$–$0.05CaTiO_3$ ceramics with 0.5 wt% WO_3 additions at different sintering temperatures.

$MgTi_2O_5$ ($\tan\delta \sim 6310^{-4}$) as well as the increase in WO_3 content. As comparing to pure 95MCT ($Q \times f \sim 55{,}000$ sintering above 1400 °C) ceramics with 0.5 wt% WO_3 addition not only lowered the sintering temperature but also possessed comparable $Q \times f$ value (~66,000 at 7 GHz). The $Q \times f$ value seemed not to obey the mixing rules, because higher formation of $CaTiO_3$ in MCT ceramics with 0.5 wt% WO_3 addition gave higher $Q \times f$ value than that with 5 wt% addition. According to previous reports, the microwave dielectric loss was simultaneously affected by many factors, mainly caused not only by the lattice vibration modes, but also by densification, pores, grain sizes and boundaries, and secondary phases. Relative density and secondary phases are important factors in controlling the dielectric loss, and has been shown for other microwave dielectric materials. Interfacial polarization is also thought to play a role in porous materials at lower sintering temperature. Because the secondary phases $CaWO_4$ with 2 wt% and 5 wt% addition, but not find with 0.5 wt% addition MCT ceramics, the secondary phases was suggested to dominate the $Q \times f$ values of MCT ceramics with WO_3 additions at lower sintering temperatures.

Fig. 6 illustrates the temperature coefficients of resonant frequency (τ_f) of 95MCT ceramics with various WO_3 additions at different sintering temperatures. The temperature coefficient of resonant frequency (τ_f) was insensitive to the sintering temperatures above 1170 °C. The τ_f values became more negative with increasing WO_3 addition. It varied from −8.2 to −22.5 ppm/°C as the amount of WO_3 addition increased from 0.5 to 5 wt% at differ-

Table 1
Simulation results of the band-pass filters using different dielectrics.

Substrate	tan δ	ε_r	Size (mm^2) $a \times b$	Insertion loss (dB)	Return loss (dB)	Fractional bandwidth (%)
Al_2O_3	0.001	9.8	15.25×21.7	2.2	15.1	8
95MCT ceramics with 0.5 wt% WO_3	0.00012	20.3	14.1×16.1	1.9	20.0	8.1

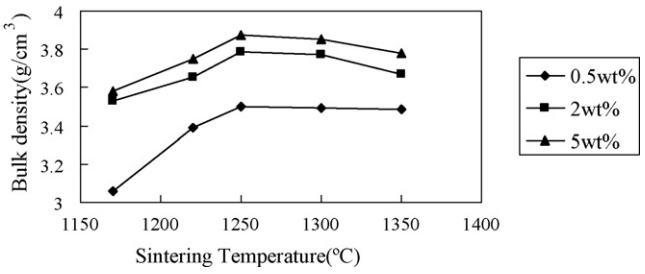

Fig. 3. Apparent density of $0.95MgTiO_3$–$0.05CaTiO_3$ ceramics with different amount of WO_3 additions as function of their sintering temperature.

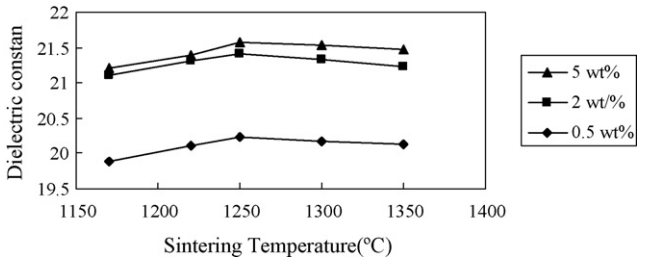

Fig. 4. ε_r value of $0.95MgTiO_3$–$0.05CaTiO_3$ system with various WO_3 addition sintered at different temperatures.

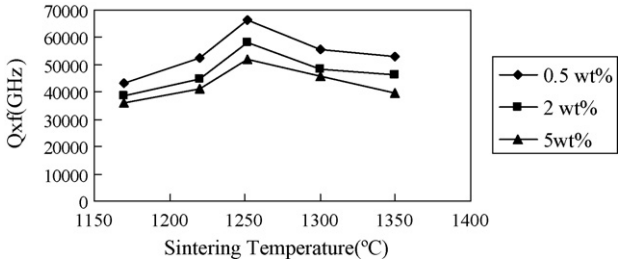

Fig. 5. $Q \times f$ values of $0.95MgTiO_3$–$0.05CaTiO_3$ system with various WO_3 additions sintered at different temperatures.

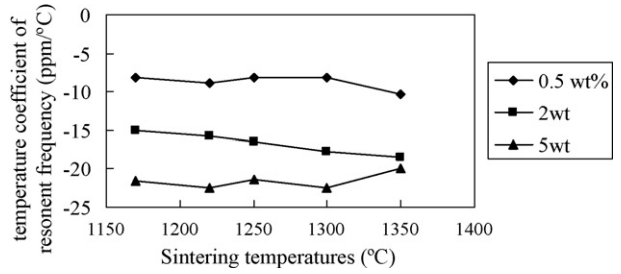

Fig. 6. τ_f values of $0.95MgTiO_3$–$0.05CaTiO_3$ system with various WO_3 addition sintered at different temperatures.

ent sintered temperature. Since the τ_f values of $MgTiO_3$ and $CaTiO_3$ are −50 and 800 ppm/°C, respectively, it implies that zero τ_f can be achieved by increasing the amount of $CaTiO_3$ content.

To verify the performance of the proposed material, a band-pass filter is designed for a center frequency of 2 GHz and fabricated on

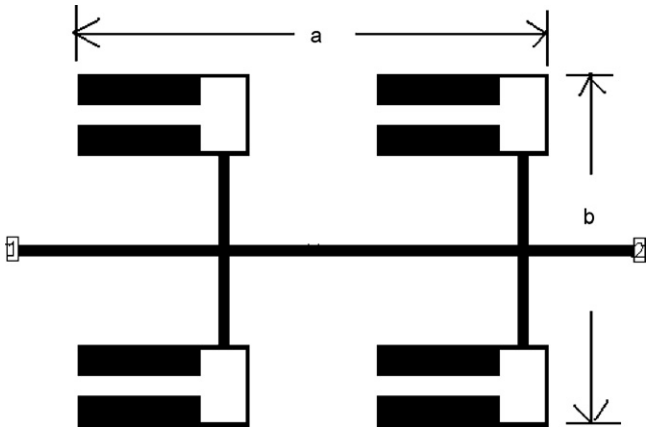

Fig. 7. Layout of the slow-wave band-pass filter.

Al_2O_3 and 95MCT. Fig. 7 shows the physical layout of the designed filter with a center frequency of 2 GHz. The simulation results are listed in Table 1. Compared to alumina, the filter using the 95MCT ceramic shows a tremendous reduction in the insertion loss and demonstrates a large reduction in its size.

4. Conclusion

WO_3 addition to $MgTiO_3$–$CaTiO_3$ ceramics not only effectively lowered the sintering temperature but also promoted its microwave dielectric properties due to the liquid phase effect. MCT ceramics showed mixed phases of $MgTiO_3$ as the main phase associated with minor phases $CaTiO_3$ and $MgTi_2O_5$. With more WO_3 additions, MCT ceramics seemed to inhibit the formation of $CaTiO_3$ but slightly enhance the formation of $MgTi_2O_5$ and second phase $CaWO_4$ was formed. The existence of $CaWO_4$ phase caused decrease in the $Q \times f$ value, which indicated that a greater WO_3 addition would increase the densification and increase the $Q \times f$ value of the ceramics. At 1250 °C, $0.95MgTiO_3$–$0.05CaTiO_3$ ceramics with 0.5 wt% WO_3 addition gave excellent microwave dielectric properties: ε_r ~20.3, $Q \times f$ value ~66,000 (at 7 GHz) and τ_f value ~−8.2 ppm/°C. Compared to alumina, the filter using 95MCT ceramics shows a tremendous reduction in the insertion loss and demonstrates a large reduction in its size.

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