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Reaction-sintering method for ultra-low loss $(Mg_{0.95}Co_{0.05})TiO_3$ ceramics

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ABSTRACT

Microwave dielectric properties and microstructures of $(Mg_{0.95}Co_{0.05})TiO_3$ ceramics prepared by a new sintering method (reaction-sintering method) were investigated. A pure phase of $(Mg_{0.95}Co_{0.05})TiO_3$ was obtained by the new method and excellent dielectric properties were observed due to uniformities of the microstructure and the phase. In contrast, the secondary phase $(Mg_{0.95}Co_{0.05})Ti_2O_5$ was observed in samples prepared by conventional sintering method. In order to study the influence of secondary phase on the microwave dielectric properties quantitatively, the weight fraction of $(Mg_{0.95}Co_{0.05})Ti_2O_5$ was calculated on the basis of Rietveld refinement. The pore-freeε_r values of specimens prepared by two different methods indicated that porosity plays an important role in the ε_r values of $(Mg_{0.95}Co_{0.05})TiO_3$ ceramics. Specimens sintered by reaction-sintering method at 1350 °C for 4 h possess excellent dielectric properties with an ε_r of 16.3, a $Q \times f$ value of 244,500 GHz, and a τ_f value of −53.5 ppm/°C.

1. Introduction

The demand for microwave dielectric ceramics with high performance in high frequency is increasing recently. A variety of microwave dielectric ceramics with high $Q \times f$ value have been intensively investigated, such as $MgTiO_3$, Mg_2TiO_4, $Ba(Mg,Ta)O_3$, $(Zr,Sn)TiO_4$, $ZnTiNb_2O_8$ [1–7]. $MgTiO_3$is one of the most popular dielectric materials for microwave devices, due to its high dielectric constant ($\varepsilon_r \sim 17$), high quality factor ($Q \times f$ value ~160,000 GHz) and negative τ_f value (−50 ppm/°C) [8]. With partial replacement of Mg^{2+} by Co^{2+}, $(Mg_{0.95}Co_{0.05})TiO_3$ ceramics ($\varepsilon_r \sim 16.8$, $Q \times f$ value ~230,000 GHz, $\tau_f \sim -54$ ppm/°C) were investigated and reported [9]. However, the experiment conditions to achieve such a high $Q \times f$ value were strict: not only high purity of raw materials but also long time sintering are needed. Researchers made effort to study the microstructures and microwave dielectric properties of $(Mg_{0.95}Co_{0.05})TiO_3$ ceramics by various methods [10–13]. In most of these researches, $(Mg_{0.95}Co_{0.05})TiO_3$ ceramics were prepared by conventional sintering (hereafter referred to as CS) route. However, the microwave dielectric properties of the result material were not so good.

Reaction-sintering (hereafter referred to as RS) has increased in popularity for its high efficiency by avoiding calcination and re-milling process. Several materials, such as $Pb(Fe_{1/2}Nb_{1/2})O_3$, $MgNb_2O_6$ and $ZnNb_2O_6$, has been successfully prepared using RS method [14,15]. Yi-Cheng Liou obtained calcium-doped $MgTiO_3$–$MgTi_2O_5$ ceramics by RS process [16]. But the presence of $MgTi_2O_5$ phase in Liou's work exerted a significant negative influence on the microwave dielectric properties of $MgTiO_3$ ceramics. In this work, $(Mg_{0.95}Co_{0.05})TiO_3$ ceramics was prepared using RS method. The resultant microwave dielectric properties were analyzed based on the X-ray diffraction patterns, densification, and the microstructures of the ceramics. The effects of porosity and phase formation on microwave dielectric properties were also discussed quantitatively. RS method was proved to be a simple and efficient method to produce pure phase $(Mg_{0.95}Co_{0.05})TiO_3$ ceramics with excellent dielectric properties.

2. Experimental

$(Mg_{0.95}Co_{0.05})TiO_3$ (95MCT) powders were prepared by mixing all the raw materials according to desired stoichiometry. The reagent grade of the oxides was listed as follow: MgO (≥98%), TiO_2 (≥99%, rutile), CoO (≥99%). Mixtures were milled in distilled water for 12 h with agent balls and then dried. For RS method, the powders were directly pressed into pellets with 10 mm in diameter and 5 mm in thickness after granulated by sieving through an 80 mesh together with the organic binder. While for CS method, the powders were calcined at 900 °C for 2 h and re-milled for 24 h before granulated and pressed. All these pellets were sintered at 1225–1400 °C for 4 h in air. The whole process of both CS and RS method is shown in Fig. 1. It is easy to see, from Fig. 1, that RS method has great advantages over CS method in simplifying the preparation technique.

The crystalline phases of the sintered ceramics were identified by X-ray diffraction pattern analysis (Rigaku D/max) using Cu K_α radiation. And the XRD pattern used for refinement was performed at a 0.02°/0.5S scanning speed. The weight fraction of main phase and secondary phase were obtained by Rietveld refinement using Fullprof [17]. Microstructure observations and analyses of sintered surfaces were performed by scanning electron microscopy (Philips XL30E) associated with energy dispersive spectroscopy (EDS). The apparent densities of the sintered pellets were measured by the Archimedes method (Mettler Toledo XS64).

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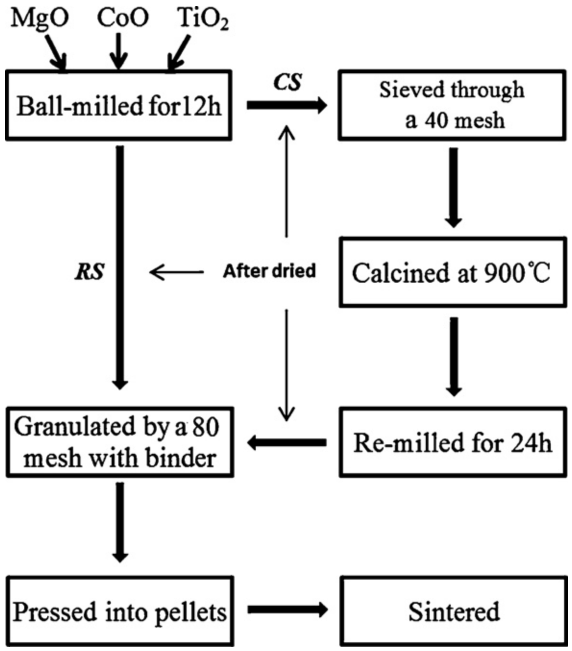

Fig. 1. Reaction-sintering and conventional sintering process for $(Mg_{0.95}Co_{0.05})TiO_3$ ceramics.

The dielectric constant ε_r and the quality value Q at microwave frequency was measured by the modified Hakki-Coleman's method [18] and the cavity method [19] in the $TE_{01\sigma}$ mode using Agilent 8720ES network analyzer. The temperature coefficient of resonant frequency (τ_f) was calculated using the equation

$$T_f = \frac{f_{85} - f_{25}}{f_{25} \times 60}$$

where f_{85} and f_{25} are the $TE_{01\sigma}$ resonant frequency of the samples at 85 °C and 25 °C, respectively.

3. Results and discussion

3.1. XRD analysis and quantitative determination

Fig. 2(a) shows the XRD patterns of 95MCT ceramics prepared by CS method sintered at 1275 °C and RS method sintered at 1350 °C, respectively. No secondary crystalline phase is found to coexist with the main phase $(Mg_{0.95}Co_{0.05})TiO_3$ (which can be indexed as $MgTiO_3$: ICDD #06-0494) in RS specimen, while a secondary phase $(Mg_{0.95}Co_{0.05})Ti_2O_5$ (ICDD #35-0796) is observed in the XRD pattern of CS-prepared sample. It indicates that $MgTi_2O_5$ is difficult to eliminate from $MgTiO_3$ prepared by conventional mixed oxide route [20]. Fig. 2(b) shows the XRD pattern of $(Mg_{0.95}Co_{0.05})TiO_3$ powder prepared by CS method calcined at 900 °C. Unlike Baek's research [21], TiO_2 is recognized as a second phase in $(Mg_{0.95}Co_{0.05})TiO_3$ powder. This small amount of TiO_2 would react with $(Mg_{0.95}Co_{0.05})TiO_3$ to form $(Mg_{0.95}Co_{0.05})Ti_2O_5$ during sintering process.

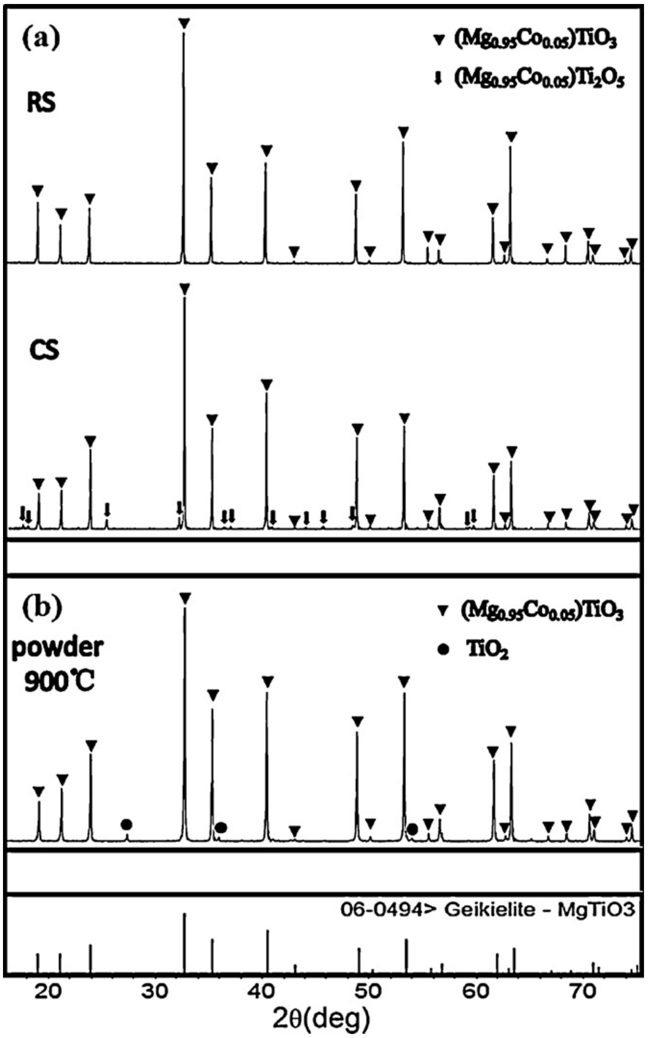

Fig. 2. X-ray diffraction patterns of RS-prepared, CS-prepared $(Mg_{0.95}Co_{0.05})TiO_3$ ceramics and CS-prepared powder.

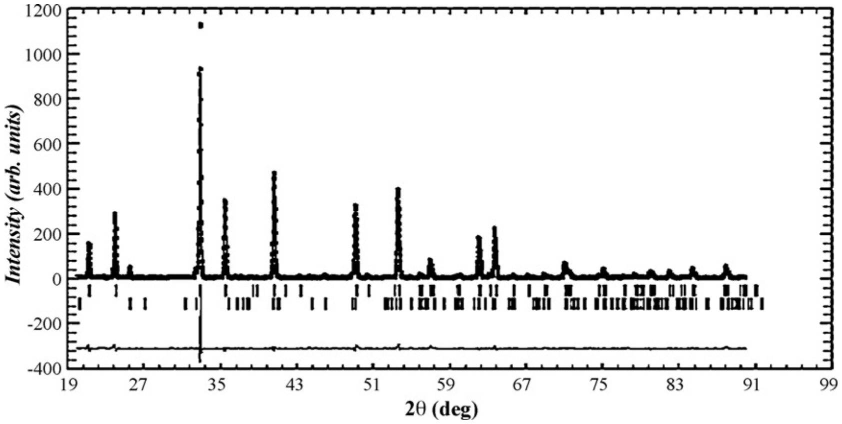

Fig. 3. Observed and calculated X-ray diffraction pattern by Rietveld analysis for CS-prepared $(Mg_{0.95}Co_{0.05})TiO_3$ specimen.

Table 1
Weight and volume fraction of $(Mg_{0.95}Co_{0.05})TiO_3$ and $(Mg_{0.95}Co_{0.05})Ti_2O_5$ obtained from Rietveld Refinement for CS sample.

	Phases	wt. fraction	vol. fraction
CS sample	$(Mg_{0.95}Co_{0.05})TiO_3$	95.79%	95.52%
	$(Mg_{0.95}Co_{0.05})Ti_2O_5$	4.21%	4.48%

Rp = 8.22%, Rwp = 13.0%, GOF = 0.2661.

Fig. 3 shows the result of Rietveld refinement analyses of X-ray diffraction pattern for CS-prepared specimen sintered at 1275 °C. The weight fraction together with the volume fraction which calculated from the weight fraction and theoretical density are listed in Table 1. The weight fraction was calculated directly from scale factors which obtained by the quantitative phase analysis using the Rietveld refinement [17]. A pseudo-Voight function was used to model the shape of the diffraction peaks. All parameters of interest including background, zero-point, scale factors for all phases, half-width, asymmetry parameters, unit-cell parameters, atomic positional coordinates, temperature factors were refined step-by-step for avoiding correlations. As we can see from Table 1, the volume fraction of the secondary phase $(Mg_{0.95}Co_{0.05})Ti_2O_5$ was 4.48%. This small amount of secondary phase would have effect on the microwave dielectric properties of the CS-sintered specimens.

3.2. Microstructure analysis

SEM photographs of RS-prepared 95MCTceramicssintered at different temperatures are shown in Fig. 4. A porous microstructure was observed for the specimen sintered at 1275 °C. The grain size increased with the increase of sintering temperature, and a significant increase in the grain size was observed at 1350 °C. When the temperature reached 1375 °C, a slight porous microstructure appeared due to the abnormal grain growth. Porosity and abnormal grain growth may directly affect the microwave dielectric properties of the ceramic samples. The SEM photographs indicate that 1350 °C should be an appropriate firing temperature for RS-prepared specimens.

The firing temperature for CS-prepared specimens is 1275 °C which can be confirmed by Fig. 5. The 95MCT ceramics prepared by CS method were not dense and the grains did not grow well before 1275 °C. The grain surfaces of CS samples sintered at higher temperatures were dotted with some micro particles. These particles were recognized as the second phase $(Mg_{0.95}Co_{0.05})Ti_2O_5$ according to XRD patents shown in Fig. 2. In order to confirm this judgment, Energy Dispersive Spectrometer (EDS) analysis of1325 °C sintered CS specimen was performed, and the corresponding data is presented in Table 2. The results indicate that the micro particles (spot A, (Mg + Co):Ti ≈ 1:2) were $(Mg_{0.95}Co_{0.05})Ti_2O_5$ and large grains (area B, (Mg + Co):Ti ≈ 1:1) were $(Mg_{0.95}Co_{0.05})TiO_3$. These results are in good agreement with the XRD patterns of Fig. 2.

3.3. Microwave dielectric properties analysis

The apparent densities and microwave dielectric properties of 95MCTceramics sintered at the various temperatures are shown in Fig. 6. The densities increased with increasing sintering temperature for both CS-prepared and RS-prepared specimens. After reaching their maximum at 1275 °C for CS specimen and 1350 °C for RS specimen respectively, the densities started to decrease slightly. Moreover, the shrinkage percentages and relative densities for 95MCT pellets are demonstrated in Table 3. The shrinkage percentages of CS-prepared specimens were smaller than that of RS-prepared samples, but the densities and relative densities were much larger as demonstrated in Fig. 6 and Table 3. The factors contributing to this abnormal phenomenon are the calcination at 900 °C and the re-milling for 24 h in CS process. The essence of the calcination is to form a pre-phase (sometimes called precursor) of 95MCTand to avoid the formation of closed pores and cracks caused by rapid shrinking during sintering. The closed pores and cracks directly result in the decrease of density. Mechanical activation for 24 h would lead to a temperature drop and time reduction for 95MCT sintering according to V.Petrović's research [22]. These two factors are also the main reasons why 95MCT ceramics prepared by CS method not only possessed higher dielectric constant but also had lower sintering temperature than RS-prepared ceramics.

As shown in Fig. 6, the ε_r values of the two different method prepared samples present a similar tendency with apparent densities. It indicates that the ε_r values of 95MCT ceramics is closely related to the apparent density. With increasing sintering temperature, the boundaries and pores (whose ε_r near to 1) decreased while the density increased, so the dielectric constant of samples increased. However, abnormal grain growth and pores at higher temperature decreased the density, and thus ε_r decreased. A ε_r of 17.78 was obtained for the CS-prepared specimen at 1275 °C,

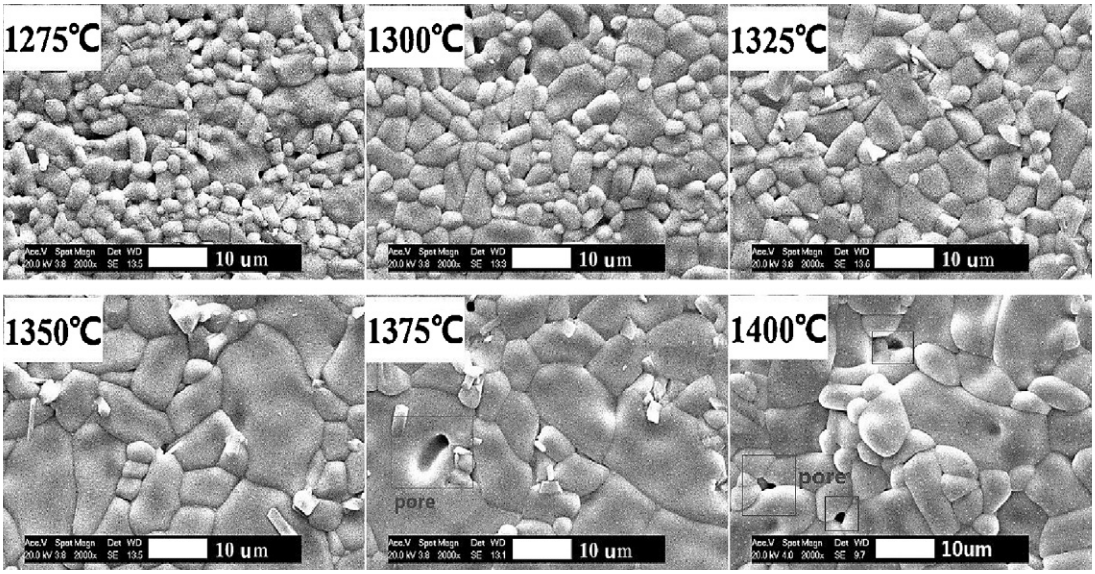

Fig. 4. SEM photographs of RS-prepared $(Mg_{0.95}Co_{0.05})TiO_3$ ceramics sintered at different temperature.

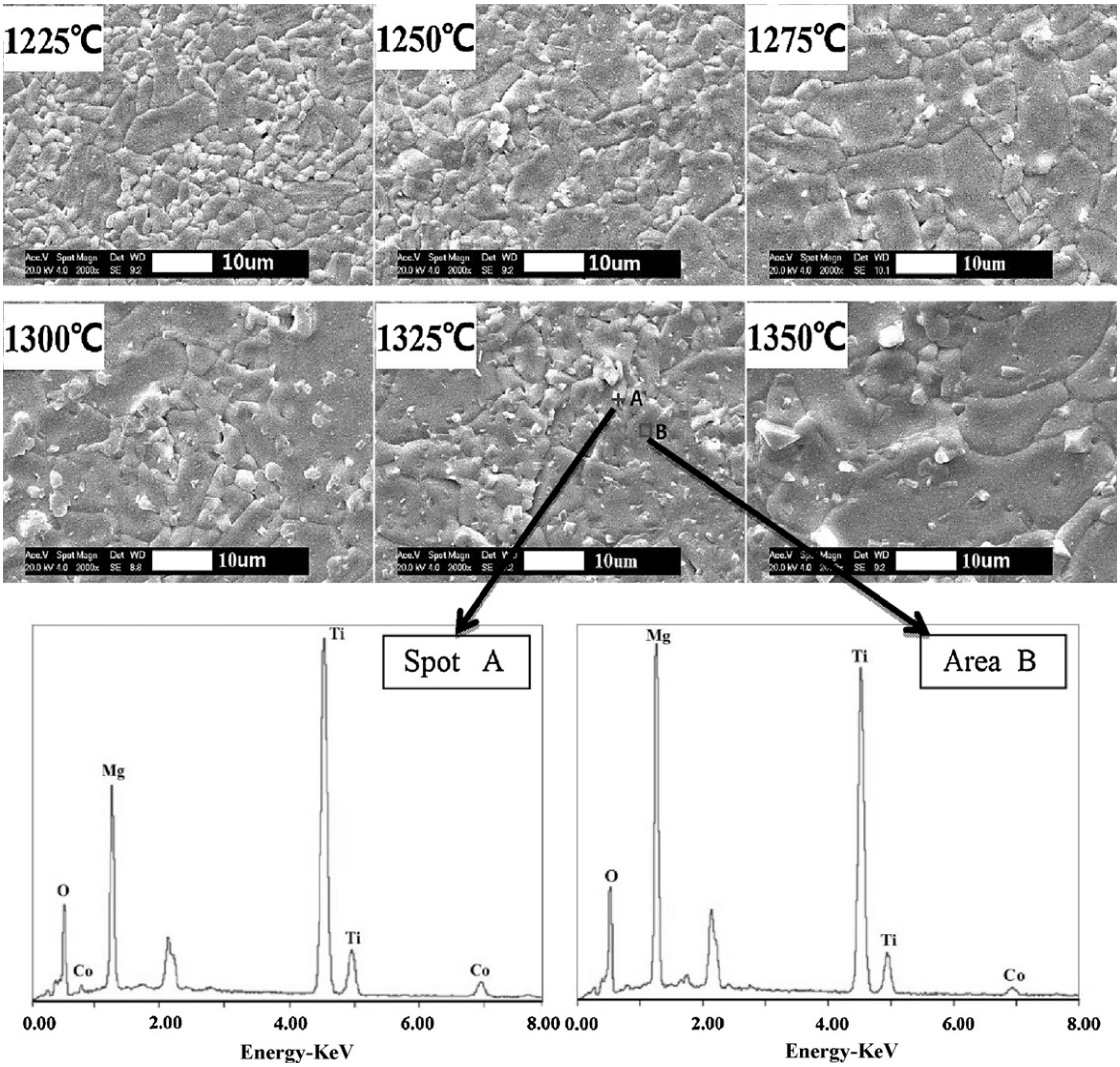

Fig. 5. SEM photographs and Energy Dispersive Spectrometer (EDS) of CS-prepared $(Mg_{0.95}Co_{0.05})TiO_3$ ceramics.

while for RS-prepared sample at 1350 °C the ε_r was only 16.3. This is mainly because the densities of RS samples are much lower than that of CS samples as discussed above. In addition (Mg, Co), Ti_2O_5 is one of the three phases formed in the MgO–CoO–TiO_2 system and the dielectric properties of $(Mg_{0.95}Co_{0.05})Ti_2O_5$ are $\varepsilon_r \sim 18.58$, $Q \times f \sim 68{,}000$ GHz and $\tau_f \sim -38.9$ ppm/°C [23]. According to Lichtenecker's mixture formula,

$$\ln \varepsilon = V_1 \ln \varepsilon_1 + V_2 \ln \varepsilon_2$$

$$\tan \delta = V_1 \tan \delta_1 + V_2 \tan \delta_2$$

the presence of $(Mg_{0.95}Co_{0.05})Ti_2O_5$ in CS samples would lead to a rise in ε_r values. The measured and calculated ε_r values using Lichtenecker's mixture formula are shown in Table 4. Moreover, the pore-free dielectric constants were also obtained [24] and shown in Table 4. Pore-free ε_r values are much higher than measured dielectric constants for both samples. And the two kinds of samples almost shared a same value of pore-free dielectric constant. This result indicates that the presence of pores have a great effect on the dielectric constant of a ceramic, while a small amount of second phase makes little contribute to the variation of ε_r values, especially when the ε_r values of the main phase and second phase have no big difference.

The relationships between $Q \times f$ values and sintering temperatures also revealed the same trend with those between densities and temperatures. With increasing sintering temperature, the $Q \times f$ values of both CS-prepared and RS-prepared specimens were found to increase to a maximum value and thereafter decrease. But unlike ε_r values, $Q \times f$ values of RS-prepared specimens were much higher than that of CS-prepared samples.

It was reported that many factors have effect on the microwave dielectric loss (low dielectric loss means high $Q \times f$ values). The intrinsic loss is generally regarded as the lower limit of dielectric loss and mainly caused by lattice vibration. $MgTiO_3$ has no localized 3*d* electrons and has an ordered corundum structure in which each TiO_6 octahedron layer is sandwiched between two layers of MgO_6 [9]. It was believed that these unique features qualifyMgTiO$_3$to possess low loss characteristics. Besides intrinsic loss, extrinsic loss plays a more important role in microwave dielectric loss for actual

Table 2
The EDS data of CS-prepared $(Mg_{0.95}Co_{0.05})TiO_3$ ceramics for spot A and area B.

Spot A	Atom (%)	Area B	Atom (%)
O K	36.85	O K	38.19
Mg K	21.57	Mg K	29.47
Ti K	40.73	Ti K	30.73
Co K	0.85	Co K	1.61

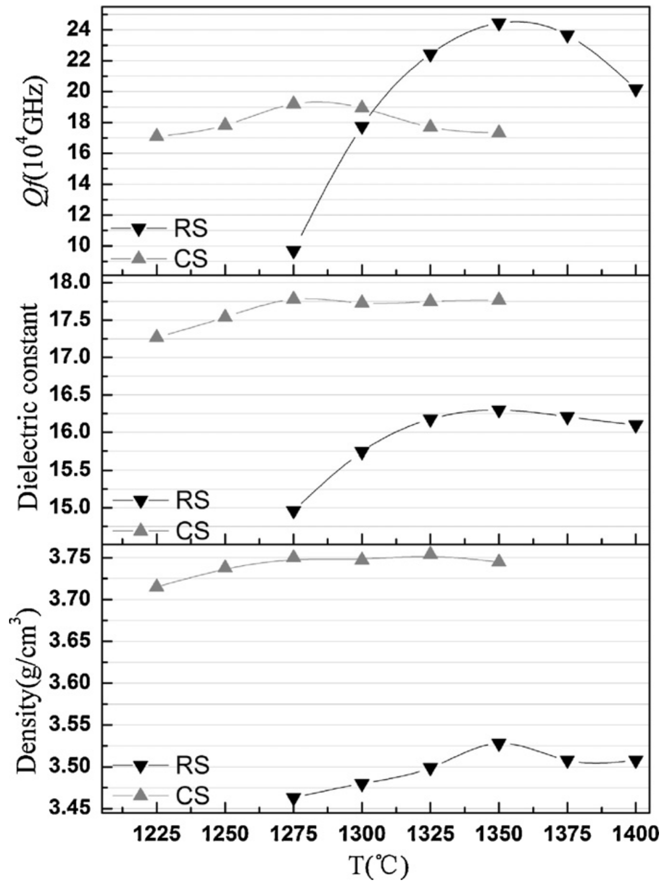

Fig. 6. Apparent density, dielectric constant and $Q \times f$ value of $(Mg_{0.95}Co_{0.05})TiO_3$ ceramics as a function of sintering temperature.

Table 3
Shrinkage percentage and relative density of $(Mg_{0.95}Co_{0.05})TiO_3$ sintered at various temperatures.

Sintering temperature (°C)	Apparent density (g/cm^3)		Relative density (%)		Shrinkage (%)	
	CS method	RS method	CS method	RS method	CS method	RS method
1225	3.715	–	94.12	–	16.56	–
1250	3.738	–	94.71	–	16.62	–
1275	3.750	3.463	95.00	87.73	16.80	19.28
1300	3.747	3.480	94.93	88.17	16.74	20.23
1325	3.754	3.499	95.11	88.64	16.77	20.21
1350	3.745	3.528	94.89	89.38	16.79	21.88
1375	–	3.508	–	88.89	–	22.20
1400	–	3.508	–	88.88	–	22.17

dielectrics. And it is mainly ascribed to undesirable second phases, lattice defects, grain boundaries, porosity, microcracks, random crystallite orientation, etc.

The variation of $Q \times f$ values for both samples with temperatures was attributed to changes in the amount of scattering caused by grain boundary and pores as temperature varies. And the gap between the $Q \times f$ values of CS and RS samples was due to the uniformity of the phase in RS specimen and the presence of secondary phase $(Mg_{0.95}Co_{0.05})Ti_2O_5$ in CS specimen as shown in Fig. 2.

The calculated $Q \times f$ values of samples prepared by CS method using Lichtenecker's mixture formula are shown in Table 4. The results, to some extent, proved that the presence of the small amount secondary phase $(Mg_{0.95}Co_{0.05})Ti_2O_5$ directly resulted in the much lower $Q \times f$ values of CS specimens than RS samples. In contrast, a $Q \times f$ value of 244,500 GHz (at 9.28 GHz) was obtained in RS-prepared 95MCT ceramic sintered at 1350 °C for 4 h.

Table 4
Measured, calculated and pore-free ε_r value, calculated $Q \times f$ value of $(Mg_{0.95}Co_{0.05})TiO_3$ prepared by RS and CS method.

Specimen	Measured ε_r	Calculated ε_r (two phase)	Pore-freeε_r	Measured $Q \times f$	Calculated $Q \times f$ (two phase)
RS (1350 °C)	16.30	–	19.11	244 500	–
CS (1275 °C)	17.78	17.81	19.14	191 900	207 800

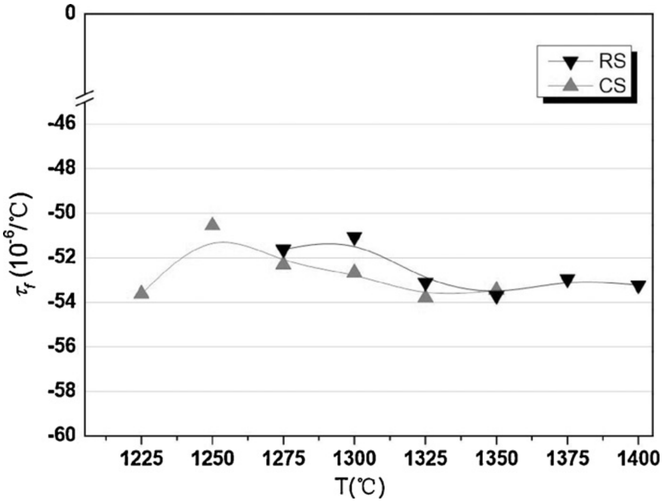

Fig. 7. τ_f values of $(Mg_{0.95}Co_{0.05})TiO_3$ ceramics sintered at different temperature.

Fig. 7 illustrates the temperature coefficient of resonant frequency (τ_f) of 95MCT. Both the two kinds of specimens possess negative τ_f values, and no significant change in τ_f values (around −51 ppm/°C to −57 ppm/°C) was observed as sintering temperature varies. The τ_f is well known to be related to the composition and the second phase of a ceramic. The presence of $(Mg_{0.95}Co_{0.05})Ti_2O_5$, whose τ_f value is compatible with that of the main crystalline phase, shows no great influence on the τ_f values of CS samples as shown in Fig. 7. And from the discussion on the $Q \times f$ values of CS samples above, we tentatively put forward that it is hard to adjust the τ_f value of a ceramic by introducing another phase (possessing a compensating τ_f value, but a low $Q \times f$ value) without decreasing the original $Q \times f$ value.

4. Conclusions

$(Mg_{0.95}Co_{0.05})TiO_3$ ceramics have been obtained successfully via reaction-sintering method. No secondary phase was found in the main crystalline phase $(Mg_{0.95}Co_{0.05})TiO_3$ for RS-prepared specimen while a minor secondary phase $(Mg_{0.95}Co_{0.05})Ti_2O_5$ was observed in CS-prepared sample. The weight fraction of $(Mg_{0.95}Co_{0.05})Ti_2O_5$ in CS sample is 4.21%. Because of the presence of second phase, the $Q \times f$ value of CS sample is lower than that of RS sample. Pore-free ε_r value of RS sample is much higher than measuredε_r due to the low relative density in RS sample. We confirmed that for the $(Mg_{0.95}Co_{0.05})TiO_3$ ceramics, the secondary phase has more influence on the $Q \times f$ values than the density. On the contrary, the density plays a more important role in ε_r values than the secondary phase, especially when the fraction of secondary phase is small.

A fine combination of microwave dielectric properties ($\varepsilon_r \sim$ 16.3, $Q \times f$ value ∼244,500 GHz, andτ_f value ∼−53.5 ppm/°C) was obtained for RS-prepared $(Mg_{0.95}Co_{0.05})TiO_3$ ceramics sintered at 1350 °C for 4 h. Reaction-sintering method was proved to be a simple and efficient method to produce pure phase $(Mg_{0.95}Co_{0.05})TiO_3$ ceramics with excellent microwave dielectric properties using ordinary analytical reagent.

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