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Structure and properties analysis for low-loss $(Mg_{1-x}Co_x)TiO_3$ microwave dielectric materials prepared by reaction-sintering method

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Abstract

$(Mg_{1-x}Co_x)TiO_3$ ($x = 0.00$–0.09) ceramics were prepared by reaction sintering method. The correlations of crystal structure and the properties were analyzed on the basis of Rietveld refinement for specimens with different x. For $x \leq 0.5$, solid solution phases with the ilmenite structure were obtained, which can be confirmed by the X-ray diffraction patterns and the lattice parameters measured. Whereas for $x > 0.05$, secondary phase was detected besides the main phase. Dielectric properties were closely related with theoretical dielectric polarizabilities, packing fraction and average octahedral distortion. By increasing x from 0.00 to 0.09, the $Q \times f$ value of the specimen decreased from a maximum of 289,400 GHz to 228,100 GHz. A fine combination of microwave dielectric properties ($\varepsilon_r \sim 16.1$, $Q \times f \sim 289{,}400$ GHz, $\tau_f \sim -54.4 \times 10^{-6}$/°C) was achieved for $MgTiO_3$ ceramics sintered at 1350 °C for 4 h.

Keywords: High Q; Reaction sintering; Crystal structure; Dielectric property

1. Introduction

The appearance of microwave dielectric ceramics greatly promoted the development of microwave integrated circuits industry. With the rapid development of wireless communication system, dielectrics with high $Q \times f$ values become more and more popular because the carrier frequencies of signals extend to higher frequency bands. The $Q \times f$ value of a material was regarded as a constant in the microwave and millimeter wave regions. Thus, higher $Q \times f$ means lower loss at a fixed frequency f [1].

$MgTiO_3$ reportedly possesses high dielectric constant of 17, high $Q \times f$ value of 160,000 GHz and negative τ_f value (-50×10^{-6}/°C) [2]. With partial replacement of Mg^{2+} by A ($A = Co^{2+}$, Mn^{2+} or Zn^{2+}), $(Mg_{0.95}A_{0.05})TiO_3$ ceramics prepared by conventional sintering method showed a much higher $Q \times f$ value (220,000–264,000 GHz) than pure $MgTiO_3$ [3,4]. The reasons for such a boost in $Q \times f$ value were not clearly discussed. Kim fully discussed the structure of $ATiO_3$ (A = Mg, Mn, Ni, Co), but specimens with substitution of A ions were not mentioned [5–7]. Hence, it is necessary to investigate and clarify the relationship between the dielectric properties and the structure as a slight substitution of A ions for Mg^{2+} ions below solid solubility.

Meanwhile, reaction sintering method (hereafter referred to as 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 microwave dielectric properties [8]. The advantage of RS method was indicated in the mentioned work, but only quantitative phase composition analysis was conducted. Therefore, structure analysis should be performed to fully understand the superiority of RS method.

In this study, $(Mg_{1-x}Co_x)TiO_3$ ($x = 0.00$–0.09) ceramics were prepared by RS method. Pure $MgTiO_3$ with no Co^{2+} substitution was found to possess the highest $Q \times f$ value in the x range of 0.00–0.09, which was distinguished from samples prepared by conventional sintering method (hereafter referred to as CS method). The reasons were discussed based on the phase composition, densification, polarizabilities, packing fraction and octahedral distortion.

2. Experimental

$(Mg_{1-x}Co_x)TiO_3$ ceramics were prepared by RS method. Reagent-grade MgO, TiO_2, CoO were weighed according to

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desired stoichiometry, ball-milled in distilled water for 12 h and then dried. The dried powders were directly pressed into pellets with 10 mm in diameter and 4–5 mm in thickness after granulated by sieving through an 80 mesh together with the organic binder. All these pellets were sintered at 1275–1375 °C for 4 h in air, using a heating rate of 5 °C/min.

The phase identification and crystal structure analysis of the sintered ceramics were carried out by X-ray diffraction method (Rigaku D/max) using Cu Kα radiation at a 0.02°/0.5 s scanning speed. The lattice parameters, unit cell volumes and atomic positions were obtained from Rietveld refinements of XRD patterns using the Fullprof program. Microstructure observations and analyses of sintered surfaces were performed by field emission scanning electron microscopy (FESEM, FEI Nanosem 430) associated with Energy Dispersive X-ray Detector (EDX, Oxford INCA). The apparent densities of the sintered pellets were measured by the Archimedes method (Mettler Toledo XS64).

The dielectric characteristics of ε and Q were examined using the modified Hakki–Coleman's method and the cavity method in the $TE_{01\sigma}$ mode on an Agilent 8720ES network analyzer. The τ_f of specimens were measured by the same method in the temperature range from 25 to 85 °C.

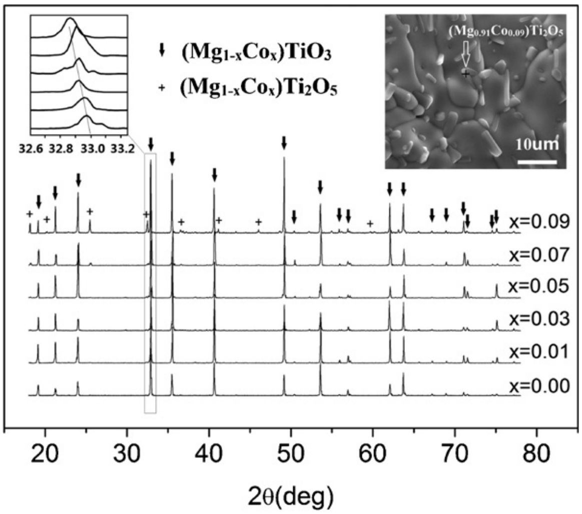

Fig. 1. Powder XRD patterns of $(Mg_{1-x}Co_x)TiO_3$ ($x = 0.00$–0.09) sintered at 1350 °C for 4 h.

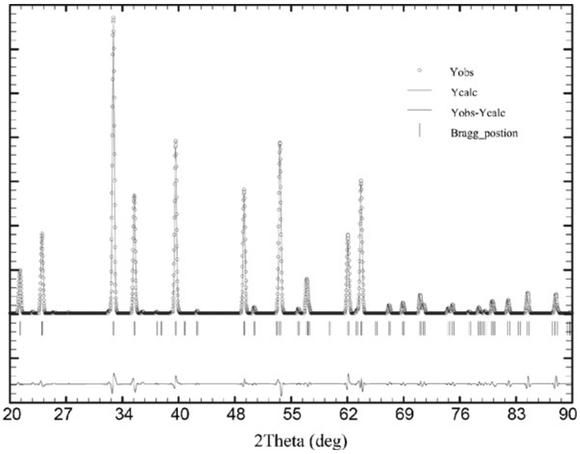

Fig. 2. Observed and calculated X-ray diffraction pattern by Rietveld analysis for $MgTiO_3$ specimen sintered at 1350 °C.

3. Results and discussion

3.1. XRD analysis and quantitative determination

The powder XRD patterns of $(Mg_{1-x}Co_x)TiO_3$ ceramics ($x = 0.00$, 0.01, 0.03, 0.05, 0.07 and 0.09) sintered at 1350 °C for 4 h are shown in Fig. 1. Fig. 2 shows the result of Rietveld refinement analysis of X-ray diffraction pattern for $MgTiO_3$ specimen sintered at 1350 °C. The crystallographic parameters obtained from the Rietveld refinement are summarized in Table 1. From Fig. 1, it is obvious that when $x \leq 0.05$, a single phase of ilmenite structure (R3-H) was confirmed. And all the XRD patterns are similar except for the small shift toward the lower angles with the increase in the value of x, which indicated that the unit cell volume increased with the increase of Co content. This is in agreement with crystallographic parameters shown in Table 1. The unit cell volume increased from 307.8276 Å^3 in $MgTiO_3$ to 308.3269 Å^3 in $(Mg_{0.95}Co_{0.05})TiO_3$. Meanwhile, the lattice parameters increased from $a = b = 5.0555$ Å, $c = 13.9072$ Å in $MgTiO_3$ to $a = b = 5.0581$ Å, $c = 13.9149$ Å in $(Mg_{0.95}Co_{0.05})TiO_3$. This is due to the fact that the ionic radii of Co^{2+} (0.745 Å) are larger than that of Mg^{2+} (0.72 Å) at the same coordination number of 6 [9]. The increase in lattice parameters and unit cell volume indicated the formation of $(Mg_{1-x}Co_x)TiO_3$ solid solution (which can be indexed as $MgTiO_3$: ICDD #06-0494).

When $x = 0.07$, secondary phase $(Mg_{1-x}Co_x)Ti_2O_5$ (ICDD #35-0796) is observed. And when $x = 0.09$, the amount of

Table 1
Lattice parameters and unit cell volume of the $(Mg_{1-x}Co_x)TiO_3$ ceramics.

x in $(Mg_{1-x}Co_x)TiO_3$	Lattice parameters of main phase $(Mg_{1-x}Co_x)TiO_3$			Lattice parameters of secondary phase $(Mg_{1-x}Co_x)Ti_2O_5$			
	$a = b$ (Å)	c (Å)	Unit cell volume (Å^3)	a (Å)	b (Å)	c (Å)	Unit cell volume (Å^3)
0.00	5.0555	13.9072	307.8276	–	–	–	–
0.01	5.0562	13.9113	308.0578				
0.03	5.0565	13.9123	308.0788				
0.05	5.0581	13.9149	308.3269				
0.07	5.0589	13.9226	308.5810	9.7393	10.0021	3.7168	363.4590
0.09	5.0642	13.9267	309.3684	9.7767	10.0447	3.7365	365.5354

secondary phase shows a significant increase (from 5.77 wt.% to 14.45 wt.%). Moreover, EDX analysis was conducted to confirm the formation of secondary phase. The bar-shaped grains shown in the SEM micrograph (sample for $x = 0.09$, sintered at 1350 °C) on the top right corner of Fig. 1 can be specified as $(Mg_{0.91}Co_{0.09})Ti_2O_5$ (Mg 19.21%, Co 1.88% Ti 38.62% O 40.29%). The presence of secondary phase would have effect on density and microwave properties.

3.2. Microwave dielectric properties analysis

The apparent densities of $(Mg_{1-x}Co_x)TiO_3$ ceramics sintered at various temperatures are shown in Fig. 3. In order to study the relative density of samples, theoretical density was calculated from the atomic weight and crystal structure by Eq. (1):

$$\rho_{\text{theory}} = \frac{ZA}{VN_A} \tag{1}$$

where $Z = 6$ is number of atoms in unit cell, A is atomic weight (g/mol), V is volume of unit cell (cm^3), N_A is Avogadro number (mol^{-1}). Then the relative densities were calculated by Eq. (2) and shown in Fig. 4. For multiphase samples, the relative densities can be calculated with mass fraction mentioned above.

$$\rho_{\text{relative}} = \frac{\rho_{\text{apparent}}}{\rho_{\text{theory}}} \tag{2}$$

The densities increased with increasing sintering temperature for all specimens. After reaching their maximum at 1350 °C, the densities started to decrease slightly. With the increase of Co content, relative densities of samples increased slightly, which indicates that the densification can be accelerated by adding CoO (see Fig. 4).

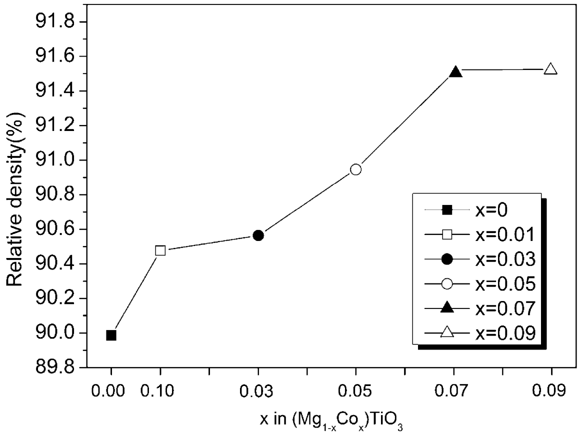

Fig. 4. Relative densities of $(Mg_{1-x}Co_x)TiO_3$ ceramics sintered at 1350 °C for 4 h.

The ε_r values of all samples present a similar tendency with apparent densities as shown in Fig. 5. The only difference was that the apparent density of $(Mg_{0.93}Co_{0.07})TiO_3$ was higher than that of $(Mg_{0.91}Co_{0.09})TiO_3$ at 1350 °C, while the ε_r value was lower (relative densities were about equal). This was because of the increasing amount of secondary phase whose density (3.643 g/cm^3) is lower while ε_r values is higher (18.58) [10]. It indicates that the ε_r value of $(Mg_{1-x}Co_x)TiO_3$ ceramics is not only related to the density but also the phase composition. On the other hand, in single phase $(Mg_{1-x}Co_x))TiO_3$ ($x \leq 0.05$), the ε_r increased from 16.1 to 16.28 as Co content increased from 0 to 0.05. When there is no secondary phase, ε_r is mainly dependent on the theoretical dielectric polarizabilities ($\alpha_{\text{theo.}}$) obtained from the additive rule shown in Eq. (3).

$$\alpha_{\text{theo.}}(ABO_3) = \alpha_A + \alpha_B + 3\alpha_O \tag{3}$$

where $\alpha_{\text{theo.}}$ is the theoretical polarizability; α_A, α_B, α_O are the ionic polarizability of A-, B-site ion, and oxygen, respectively.

From Eq. (3), the $\alpha_{\text{theo.}}$ of $(Mg_{1-x}Co_x)TiO_3$ is larger than that of $MgTiO_3$ due to the larger ion polarizabilities of Co^{2+} (1.65 Å) than Mg^{2+} (1.32 Å) [11].

Fig. 6 shows the $Q \times f$ values of $(Mg_{1-x}Co_x)TiO_3$ specimens sintered from 1275 to 1375 °C for 4 h. With increasing sintering temperature, the $Q \times f$ values of $(Mg_{1-x}Co_x)TiO_3$ specimens increased to a maximum value and thereafter decreased. Several factors contribute to the dielectric loss ($1/Q$) at

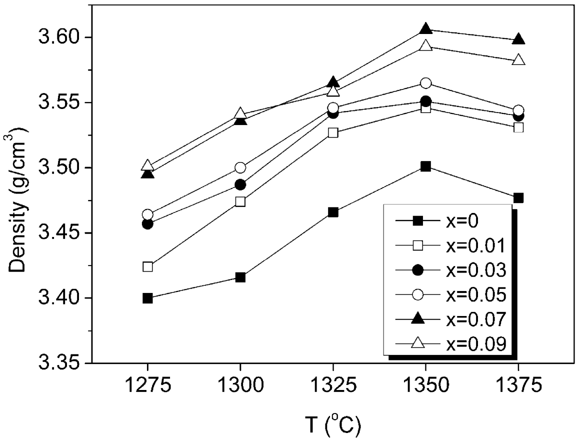

Fig. 3. Apparent densities of $(Mg_{1-x}Co_x)TiO_3$ ceramics sintered at 1275–1375 °C for 4 h.

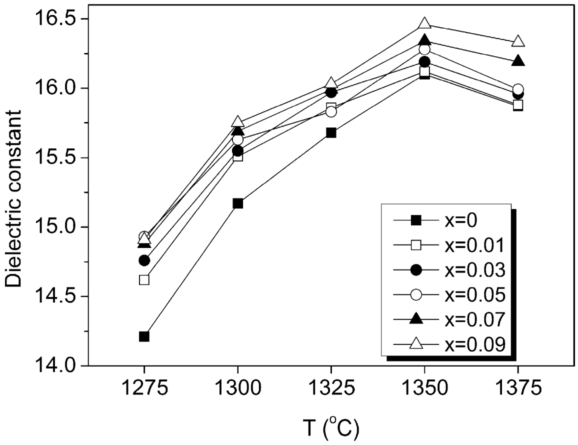

Fig. 5. Dielectric constant of $(Mg_{1-x}Co_x)TiO_3$ ceramics sintered at 1275–1375 °C for 4 h.

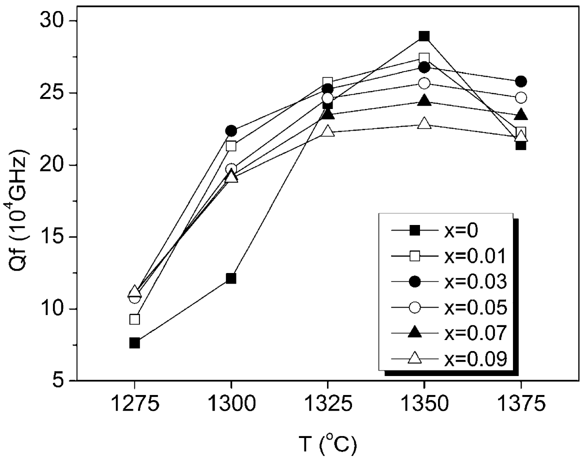

Fig. 6. $Q \times f$ values of $(Mg_{1-x}Co_x)TiO_3$ ceramics sintered at 1275–1375 °C for 4 h.

microwave frequencies, such as density, porosity, second phases, grain boundaries, and inclusions in real homogeneous ceramics. The variation of $Q \times f$ values with sintering temperature was attributed to the changes in the amount of scattering caused by grain boundary and pores. When $x = 0.07$ and 0.09, the presence of secondary phase decreased the $Q \times f$ value. And when $x \leq 0.05$, the $Q \times f$ values of $(Mg_{1-x}Co_x)$-$)TiO_3$ at each temperature decreased with the increase of Co content. Because there was no secondary phase (Fig. 1), the relationships between the crystal structure and $Q \times f$ values of $(Mg_{1-x}Co_x)TiO_3$ ($x = 0$, 0.01, 0.03, 0.05) ceramics should be considered. It is reported that the $Q \times f$ value is closely related to the packing fraction of structure [12].

$$\text{packing fraction}\,(\%) = \frac{\text{volume of the atoms in the cell}}{\text{volume of primitive unit cell}}$$
$$= \frac{\text{volume of the atoms in the cell}}{\text{volume of unit cell}} \times Z$$
$$= \frac{4\pi/3 \times (r_A^3 + r_B^3 + 3 \times r_O^3)}{\text{volume of unit cell}} \times 6 \tag{4}$$

where r_A, r_B and r_O are the effective ionic radii at each coordination number, $Z = 6$ is the number of formula units per unit cell.

As shown in Table 2, packing fractions of $(Mg_{1-x}Co_x)TiO_3$ obtained from Eq. (4) decreased with the increasing Co content. Thus, the $Q \times f$ value decreased with the decrease of packing fraction.

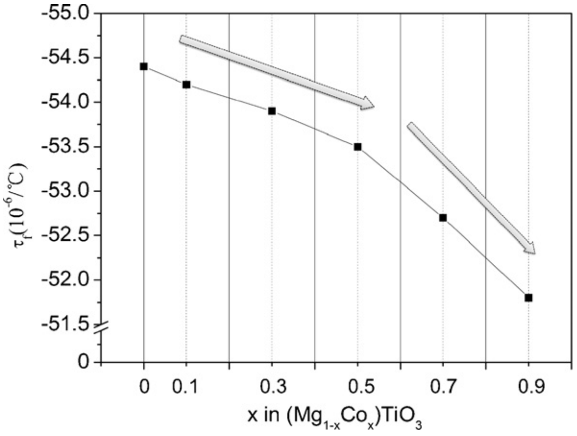

Fig. 7. τ_f values of $(Mg_{1-x}Co_x)TiO_3$ ceramics with different x sintered at 1350 °C.

Fig. 7 illustrates the temperature coefficient of resonant frequency (τ_f) of $(Mg_{1-x}Co_x)TiO_3$ ceramics sintered at 1350 °C for 4 h. The τ_f of samples sintered at 1350 °C were chosen because 1350 °C was the appropriate firing temperature and τ_f showed no big difference as sintering temperature varied [8]. With the increase of Co content, τ_f values increased from -54.4×10^{-6}/°C to -51.8×10^{-6}/°C. Generally, τ_f is related to the composition and the second phases that are present in the ceramics. The presence of second phase $(Mg_{1-x}Co_x)Ti_2O_5$ (when $x = 0.07$, 0.09) increased the τ_f value from -53.5×10^{-6}/°C to -51.8×10^{-6}/°C, because τ_f value of the second phase is more positive than the main crystalline phase [10]. When $x \leq 0.05$, there was no second phase in $(Mg_{1-x}Co_x)TiO_3$, thus the τ_f value was mainly influenced by the structure. Table 2 summarizes the average octahedral distortion and τ_f values of $(Mg_{1-x}Co_x)TiO_3$ specimens. The average octahedral distortion can be obtained from Eq. (5) [9].

$$\Delta = \frac{1}{6}\sum_{I=1}^{6}\left(\frac{R_i - \overline{R}}{\overline{R}}\right)^2 \tag{5}$$

where $\overline{R}$ is the average bond length, and R_i is an individual bond length calculated from the lattice parameters and atomic positions using fullprof.

With the increasing amount of Co content, the τ_f values of the specimens moved toward positive due to the decrease of average octahedral distortion. These results indicated that τ_f value of $(Mg_{1-x}Co_x)TiO_3$ ilmenite titanate depended on the octahedral distortion.

Table 2
Packing fraction and $Q \times f$ value, average octahedral distortion and τ_f value of $(Mg_{1-x}Co_x)TiO_3$ sintered specimens.

x in $(Mg_{1-x}Co_x)TiO_3$	Packing fraction (%)	$Q \times f$ value (10^4GHz)	A-site octahedral distortion ($\Delta_A \times 10^3$)	Ti-site octahedral distortion ($\Delta_{Ti} \times 10^3$)	Average octahedral distortion ($\Delta \times 10^3$)	τ_f value (10^{-6}/°C)
0.00	69.289	28.94	0.852	3.773	2.3125	−54.4
0.01	69.237	27.41	0.851	3.765	2.3080	−54.2
0.03	69.233	26.78	0.850	3.762	2.3060	−53.9
0.05	69.199	25.67	0.841	3.764	2.3025	−53.5
0.07	Two phase					
0.09	Two phase					

4. Conclusions

The structure and microwave dielectric properties of $(Mg_{1-x}Co_x)TiO_3$ ceramics prepared by RS method have been investigated in this paper. For $x \leq 0.05$, single phase and forming of solid solution was conrmed by the XRD analysis, the measured lattice parameter, and the unit cell volume. Secondary phase $(Mg_{1-x}Co_x)Ti_2O_5$ was observed in samples with $x = 0.07$ and 0.09. The presence of second phase resulted in a slightly increase in ε_r value, a decrease in $Q \times f$ value and a more positive τ_f value. In single phase $(Mg_{1-x}Co_x)TiO_3$ ceramics, with the increasing amount of Co content, the ε_r value increased due to the larger theoretical dielectric polarizabilities of Co, the $Q \times f$ value decreased due to the decrease of packing fraction, and τ_f value moved toward positive due to the decrease of average octahedral distortion. An ε_r of 16.1, a τ_f of -54.4×10^{-6}/°C and a $Q \times f$ value of 289,400 GHz were obtained for $MgTiO_3$ ceramic sintered at 1350 °C for 4 h. Reaction sintering method and the simple composition of $MgTiO_3$ would be a good choice for high Q microwave ceramics with obvious advantages in simplifying the preparation process and optimizing the microwave dielectric properties.

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