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Phase evolution and microwave dielectric properties of TiO_2-modified $(Mg_{0.95}Co_{0.05})_2TiO_4$ ceramics

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ABSTRACT

Phase evolution and microwave dielectric properties of $(1-x)(Mg_{0.95}Co_{0.05})_2TiO_4$–$xTiO_2$ ($x=0$–1) ceramics prepared by the conventional mixed oxide route have been investigated. Increasing the TiO_2 content would lead to a main phase transformation from $(Mg_{0.95}Co_{0.05})_2TiO_4$ to $(Mg_{0.95}Co_{0.05})TiO_3$, $(Mg_{0.95}Co_{0.05})Ti_2O_5$ and then TiO_2. Not only did the TiO_2 addition compensate the τ_f, it also lowered the sintering temperature of specimen. A huge drop of $Q\times f$ occurs at a 40–60 mol% TiO_2 addition was attributed to the formation of $(Mg_{0.95}Co_{0.05})Ti_2O_5$ phase. Specimen with $x=0.78$ can possess an excellent combination of microwave dielectric properties: $\varepsilon_r\sim 24.77$, $Q\times f\sim 38{,}500$ GHz and $\tau_f\sim -1.3$ ppm/°C.

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 patch antennas. Requirements for these dielectric materials must satisfy three main criteria: a high-relative-permittivity for miniaturization, a low dielectric loss (high $Q\times f$) for better selectivity and a near-zero temperature coefficient of resonant frequency (τ_f) for stable frequency stability for use in electronic circuits at microwave frequency [1]. Research for new materials with such an optimum combination has been ongoing and reported in these few years [2–8].

Microwave dielectric properties of binary titanate ceramic Mg_2TiO_4 was first reported by Belous et al. [3,4]. It was found to possess an extremely high $Q\times f$ of 150,000 GHz. In particular, its low cost has received much more attention. By partially substituting Mg with Co, the $(Mg_{0.95}Co_{0.05})_2TiO_4$ ($\varepsilon_r\sim 15.7$, $Q\times f\sim 286{,}000$ GHz, $\tau_f\sim -52.5$ ppm/°C) [9] composition was found to acquire a much higher $Q\times f$ and retained compatible ε_r and τ_f compared to that of pure Mg_2TiO_4. However, it has a large negative τ_f value which needs to be modified before putting it to practical applications. Since most of the dielectric ceramics with high-relative-permittivity have positive τ_f values, it is thereby desirable to search for materials having high-relative-permittivity, high Q and negative τ_f in order to achieve this goal. Therefore, TiO_2 has often been utilized in controlling microwave dielectric properties and the sintering behavior [10–12].

In this paper, TiO_2 was employed as a sintering aid and τ_f compensator, and was added to $(Mg_{0.95}Co_{0.05})_2TiO_4$ as starting materials to further lower the sintering temperature and to improve the microwave dielectric properties of the specimens. The dielectric properties at microwave frequencies of the sintered ceramics were characterized and discussed in terms of the densification and the second phases of the specimens. In addition, the X-ray diffraction (XRD) patterning and scanning electron microscopy (SEM) analysis were also employed to study the crystal structures and microstructures of the ceramics.

2. Experimental procedure

The starting materials were high-purity oxide powders (>99.9%): MgO, CoO and rutile-TiO_2. Because MgO is hygroscopic, it was fired at 600 °C to avoid moisture contain. Stoichiometric mixtures $(Mg_{0.95}Co_{0.05})_2TiO_4$ and TiO_2 were individually prepared and ground in distilled water for 24 h in a ball mill using agate balls. The wet mixtures were dried at 100 °C, and thoroughly milled before they were calcined at 1100 °C for 4 h. The calcined powders were mixed according to the molar fraction $(1-x)(Mg_{0.95}Co_{0.05})_2TiO_4$–$xTiO_2$ ($x=0$–1) and then re-milled for 24 h. Prepared powders, together with 3 wt% of a 10% solution of PVA as a binder (Polyvinyl alcohol 500, Showa, made in Japan) was pressed into pellets with dimensions of 11 mm in diameter and 5 mm in thickness under the pressure of 200 MPa. These pellets were sintered at temperatures of 1150–1390 °C for 4 h in air. The heating rate and the cooling rate were both set at 10 °C/min.

The crystalline phases of the sintered ceramics were identified by XRD using Cu Kα ($\lambda=0.15406$ nm) radiation with a Siemens D5000 diffractometer (Munich, Germany) operated at 40 kV and 40 mA. The microstructural observation and analysis of sintered surface were performed using a scanning electron microscopy (SEM; Philips XL-40FEG, Eindhoven, the Netherlands) and an energy dispersive X-ray spectrometer (EDS). The apparent densities of the sintered pellets were measured by the Archimedes method. The relative permittivity (ε_r) and the quality factor values (Q) at microwave frequencies were measured using the Hakki–Coleman dielectric resonator method.[13,14] A system combining a HP8757D network analyzer and a HP8350B sweep oscillator (Palo Alto, CA) was employed in the measurement. For temperature coefficient of resonant frequency (τ_f), the technique is the same as that of quality factor measurement. The test cavity is placed over a thermostat and the

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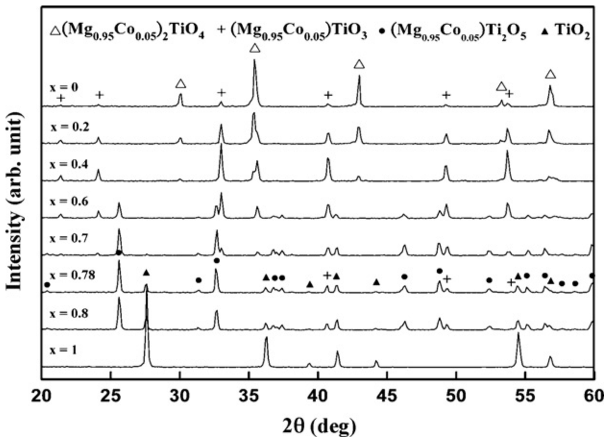

Fig. 1. X-ray diffraction patterns of $(1-x)(Mg_{0.95}Co_{0.05})_2TiO_4$–$xTiO_2$ ceramic system sintered at 1240 °C for 4 h with different x values.

temperature range used is from 20 to 80 °C. The τ_f (ppm/°C) can be calculated by noting the change in resonant frequency (Δf),

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

where f_1 is resonant frequency at T_1 and f_2 is the resonant frequency at T_2.

3. Results and discussion

Fig. 1 shows the room temperature X-ray diffraction (XRD) patterns recorded for $(1-x)(Mg_{0.95}Co_{0.05})_2TiO_4$–$xTiO_2$ ceramics sintered at 1240 °C for 4 h. The cubic-structured $(Mg_{0.95}Co_{0.05})_2TiO_4$ (can be indexed as Mg_2TiO_4, ICDD-PDF #00-025-1157) belonging to the space group Fd-3m(227) is identified as the main phase and another magnesium titanate phase of $(Mg_{0.95}Co_{0.05})TiO_3$ (can be indexed as $MgTiO_3$, ICDD-PDF #00-006-0494) is also spotted as a second phase. As the concentration of TiO_2 in $(Mg_{0.95}Co_{0.05})_2TiO_4$ increased, the $(Mg_{0.95}Co_{0.05})_2TiO_4$ disappeared and a $(Mg_{0.95}Co_{0.05})Ti_2O_5$ phase was formed consequent to the reaction between $(Mg_{0.95}Co_{0.05})TiO_3$ and TiO_2. For >70 mol% of TiO_2 addition, the presence of rutile phase was also detected in the XRD-patterns.

The relative permittivity corresponding to the phase evolution shown in Fig. 1 for $(1-x)(Mg_{0.95}Co_{0.05})_2TiO_4$–$xTiO_2$ ceramics is illustrated in Fig. 2. The variation of relative permittivity is insignificant for specimens with 0–70 mol% TiO_2 additions because the $(Mg_{0.95}Co_{0.05})_2TiO_4$ ($\varepsilon_r \sim 15.7$), $(Mg_{0.95}Co_{0.05})TiO_3$ ($\varepsilon_r \sim 16.8$) [15] and $(Mg_{0.95}Co_{0.05})Ti_2O_5$ ($\varepsilon_r \sim 18.58$) [16] phase show similar relative permittivity. The tremendous increase of the relative permittivity for $x > 0.7$ was due to the presence of TiO_2 phase, which possesses a much higher ε_r value (~98) in comparison with those of other compounds.

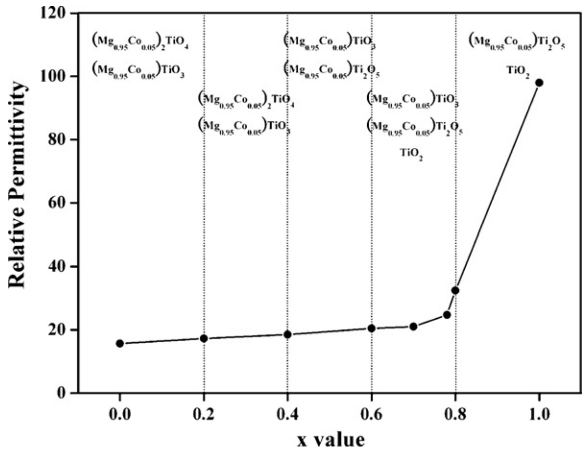

Fig. 2. Relative permittivities of $(1-x)(Mg_{0.95}Co_{0.05})_2TiO_4$–$xTiO_2$ ceramic system.

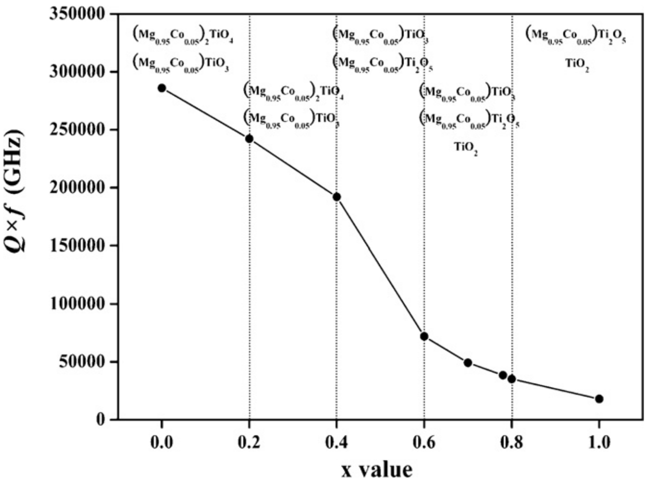

Fig. 3. $Q \times f$ values of $(1-x)(Mg_{0.95}Co_{0.05})_2TiO_4$–$xTiO_2$ ceramic system.

The $Q \times f$ value of $(Mg_{0.95}Co_{0.05})_2TiO_4$ is plotted in Fig. 3 as a function of TiO_2 content. It decreases from 286,000 GHz at $x = 0$ to 192,000 GHz at $x = 0.4$ as expected because of the decrease of $(Mg_{0.95}Co_{0.05})_2TiO_4$ ($Q \times f \sim 286{,}000$ GHz) phase, which has a higher $Q \times f$ compared to that of $(Mg_{0.95}Co_{0.05})TiO_3$ ($Q \times f \sim 230{,}000$ GHz) [15] phase. The $Q \times f$ of 192,000 GHz is still lower than that of pure $(Mg_{0.95}Co_{0.05})TiO_3$. It might be a result from the existence of a minor $(Mg_{0.95}Co_{0.05})Ti_2O_5$ ($Q \times f \sim 71{,}000$ GHz) [16] phase that is extremely difficult to detect by X-ray. However, the effect of the presence of $(Mg_{0.95}Co_{0.05})Ti_2O_5$ phase on the $Q \times f$ is significant at $x > 0.4$ and the $Q \times f$ shows a huge drop from 192,000 GHz at $x = 0.4$ to 49,200 GHz at $x = 0.7$ and then the drop becomes smooth thereafter. The variation of τ_f value (Fig. 4) was similar with that of relative permittivity because the $(Mg_{0.95}Co_{0.05})_2TiO_4$ ($\tau_f \sim -52.5$ ppm/°C), $(Mg_{0.95}Co_{0.05})TiO_3$ ($\tau_f \sim -54$ ppm/°C) [15] and $(Mg_{0.95}Co_{0.05})Ti_2O_5$ ($\tau_f \sim -38.9$ ppm/°C) [16] phase also show similar τ_f. The substantial increase of the τ_f value for $x > 0.7$ was contributed to the presence of TiO_2 phase because it has a much higher τ_f value (~420 ppm/°C) compared to those of other phases.

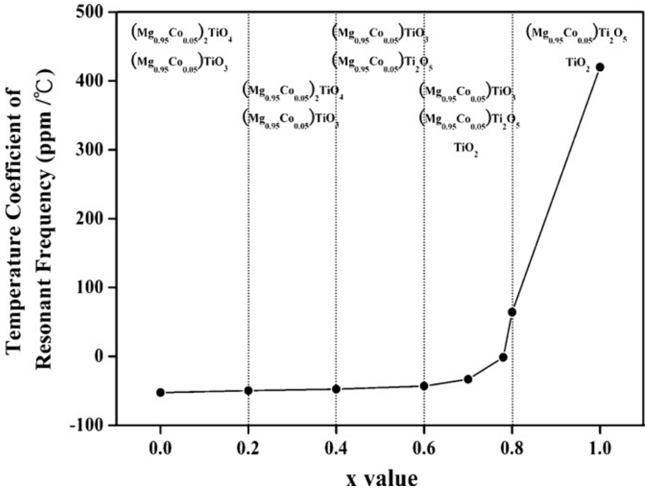

Fig. 4. τ_f values of $(1-x)(Mg_{0.95}Co_{0.05})_2TiO_4$–$xTiO_2$ ceramic system.

Table 1
Microwave dielectric properties of $(1-x)(Mg_{0.95}Co_{0.05})_2TiO_4$–$xTiO_2$ ceramic system at different sintering temperatures for 4 h.

x value	Apparent density (g/cm^3)	ε_r	$Q \times f$	τ_f (ppm/°C)	Sintering temp. (°C)
0	3.56	15.70	286,000	−52.5	1390
0.2	3.62	17.28	242,200	−49.6	1360
0.4	3.71	18.52	192,000	−47.4	1330
0.6	3.78	20.48	72,000	−43.0	1300
0.7	3.82	21.01	49,200	−33.2	1270
0.78	3.84	24.77	38,500	−1.3	1240
0.8	3.85	32.47	35,200	64.3	1240
1	4.07	98	18,000	420	1300

Table 1 summarizes the microwave dielectric properties of $(1-x)(Mg_{0.95}Co_{0.05})_2TiO_4$–$xTiO_2$ ceramics and their bulk densities and sintering temperatures are also included. Addition of $(Mg_{0.95}Co_{0.05})_2TiO_4$, having a much smaller grain size in comparison with that of TiO_2, could effectively hold back abnormal grain growth in the TiO_2 matrix. The sintering temperature of the specimen seems to be effectively lowered by increasing the TiO_2 content. Similar phenomenon was also reported for other dielectric ceramics [17,18]. Moreover, the sintering temperature for specimens with different TiO_2 additions to achieve the highest $Q \times f$ also corresponding to the highest density, suggesting the $Q \times f$ was mainly controlled by the density of specimens. It is also noteworthy to state that the dielectric properties of the specimens varied in response to the compositional ratio of the end members and at a ratio of $(Mg_{0.95}Co_{0.05})_2TiO_4$:$TiO_2$ = 22:78, a near zero τ_f can be achieved.

4. Conclusion

Phase evolution and microwave dielectric properties of $(Mg_{0.95}Co_{0.05})_2TiO_4$–$TiO_2$ ceramics have been investigated in this paper. The addition of TiO_2 can further lower the sintering temperature and also acquire higher density of the specimen. The τ_f can be precisely adjusted through the control of the TiO_2 addition. Formation of $(Mg_{0.95}Co_{0.05})Ti_2O_5$ occurs at a 40–60 mol% TiO_2 addition. A relative permittivity (ε_r) of 24.77, a high $Q \times f$ value of 38,500 GHz and a temperature coefficient of resonant frequency (τ_f) of −1.3 ppm/°C can be obtained for specimen using $0.22(Mg_{0.95}Co_{0.05})_2TiO_4$–$0.78TiO_2$ sintered at 1240 °C for 4 h.

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