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The effect of non-stoichiometry on the microstructure and microwave dielectric properties of the $Mg_{1+\delta}TiO_{3+\delta}$ ceramics

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ABSTRACT

The microwave dielectric properties and microstructure of $Mg_{1+\delta}TiO_{3+\delta}$ ($-0.05 \leq \delta \leq 0.05$) ceramics prepared via the conventional solid-state route were investigated. A slight deviation from stoichiometry does not practically affect the relative permittivity and temperature coefficient of resonant frequency of the specimen. However, the $Q \times f$ value is very sensitive to the composition and it shows a non-linear variation corresponding to a relative amount of Mg. A very high $Q \times f$ can be achieved for specimen with single $MgTiO_3$ phase, which can be obtained within the compositional range $-0.02 \leq \delta \leq 0.02$. In addition, a low $Q \times f$ measured for specimens at $\delta < -0.02$ can be attributed to the presence of second phase $MgTi_2O_5$. An extremely high $Q \times f$ of ~357,600 GHz (at 10 GHz) together with an ε_r of ~18.3 and a τ_f of ~−50 ppm/°C can be found for specimen using $Mg_{1.02}TiO_{3.02}$.

1. Introduction

There are three primary requirements for dielectric ceramics used at microwave frequencies: a high relative permittivity to reduce the size of the components, a high quality factor to increase the frequency selectivity, and a near zero τ_f to ensure high temperature stability [1]. However, as the carrier frequency is extended from 900 MHz to 2.4, 5.2, 5.8 GHz or even to the millimeter wave range, high-relative-permittivity materials become unsuitable because small-sized devices are difficult to fabricate. Low-dielectric-loss materials, on the contrary, are receiving much more attention since the $Q \times f$ value is almost constant in the microwave and millimeter wave frequency bands [1–6]. One of the superior microwave dielectrics is the complex perovskite ceramic $Ba(Mg_{1/3}Ta_{2/3})O_3$, which has a high unloaded quality factor ($Q \times f = 300{,}000$ GHz) and a high dielectric constant ($\varepsilon_r = 25$). The Q value of $Ba(Mg_{1/3}Ta_{2/3})O_3$ increases with the B-site ordering [7,8]. Although this material has excellent microwave dielectric properties, it requires a high sintering temperature (1600–1650 °C) and a long soaking time (~50 h) [9]. Moreover, the use of Ta is too expensive to put it to practical applications.

Magnesium titanate ceramics ($MgO–TiO_2$) are also popular dielectric materials for microwave frequency applications. Among them, the $MgTiO_3$ ceramic has an ilmenite-type structure, belonging to the trigonal space group $R\bar{3}$ and possesses a high dielectric constant ($\varepsilon_r \sim 17$), a high quality factor ($Q \times f \sim 160{,}000$ GHz), and a negative τ_f value (−50 ppm/°C) [10,11]. Its low cost makes them especially attractive. With the partial replacement of Mg by Zn or Co, the dielectrics $(Mg_{0.95}Co_{0.05})TiO_3$ ($\varepsilon_r \sim 16.8$, $Q \times f \sim 230{,}000$ GHz, and $\tau_f \sim -54$ ppm/°C) [12] and $(Mg_{0.95}Zn_{0.05})TiO_3$ ($\varepsilon_r \sim 17.1$, $Q \times f \sim 264{,}000$ GHz, and $\tau_f \sim -40.3$ ppm/°C) [13], also having an ilmenite-type structure, have been reported to possess excellent dielectric properties in particular high $Q \times f$ value. However, they suffered from the formation of second phases, such as $(Mg_{0.95}Zn_{0.05})Ti_2O_5$, which would degrade their dielectric properties [1,14]. Still, preparation of $MgTiO_3$ is quiet critical since Mg-deficient compound would lead to a $MgTi_2O_5$ phase while Mg-rich causes the formation of Mg_2TiO_4 phase. Non-stoichiometric effect for other compounds had been shown by Belous et al. However, the variance tolerance of the Mg content to obtain a single $MgTiO_3$ phase was not studied ever.

In this paper, the non-stoichiometric $Mg_{1+\delta}TiO_{3+\delta}$ ceramic system were prepared via the conventional solid-state route to investigate the effect of slight change in Mg content on the microwave dielectric properties, phase composition and microstructure of $MgTiO_3$ ceramic.

2. Experimental

The starting materials were high-purity oxide powders (≥99%): $MgCO_3 \cdot 0.2708H_2O$ (1 mol of $MgCO_3$ contained 0.2708 mol of moisture content, 99% purity, average particle diameter ~ 44 μm, Strem Chemical Inc., USA) and TiO_2 (99.9% purity, average particle diameter ~ 0.25 μm, Showa Chemical Co., Ltd., Japan). Typical Mass of Powder in Individual $Mg_{1+\delta}TiO_{3+\delta}$ Powder Batches is

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Table 1
Typical mass of powder in individual $Mg_{1+\delta}TiO_{3+\delta}$ powder batches.

δ value	$MgCO_3 \cdot 0.2708H_2O$ (g)	TiO_2 (g)	Total mass (g)
−0.05	51.4743	48.5257	100
−0.03	51.9946	48.0054	100
−0.02	52.2505	47.7495	100
−0.01	52.5037	47.4963	100
0	52.7543	47.2457	100
0.01	53.0022	46.9978	100
0.02	53.2476	46.7524	100
0.03	53.4904	46.5096	100
0.05	53.9685	46.0315	100

illustrated in Table 1. The decomposition reaction of $MgCO_3 \cdot xH_2O$ at temperatures of 600–700 °C for 5 h can be represented as follows:

$$MgCO_3 \cdot xH_2O \rightarrow MgO + CO_2 + xH_2O \tag{1}$$

Fig. 1(a) and (b) shows the thermal gravity analysis (TGA) and X-ray diffraction (XRD) pattern of $MgCO_3 \cdot xH_2O$ decomposed at a temperature of 650 °C for 5 h, respectively. The figure indicates that CO_2 and H_2O were entirely eliminated from $MgCO_3 \cdot xH_2O$; only residual MgO remained. From Eq. (1), the moisture content mole number can be obtained.

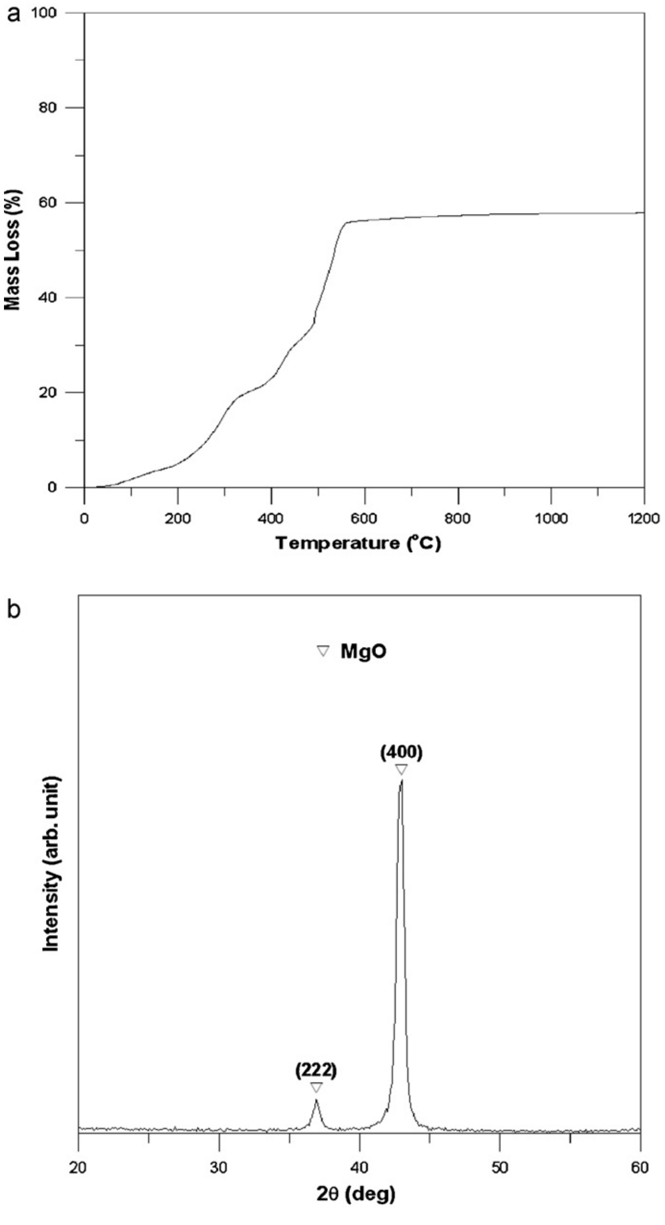

Fig. 1. (a) TGA and (b) XRD patterns of $MgCO_3 \cdot xH_2O$ decomposed at 650 °C for 5 h.

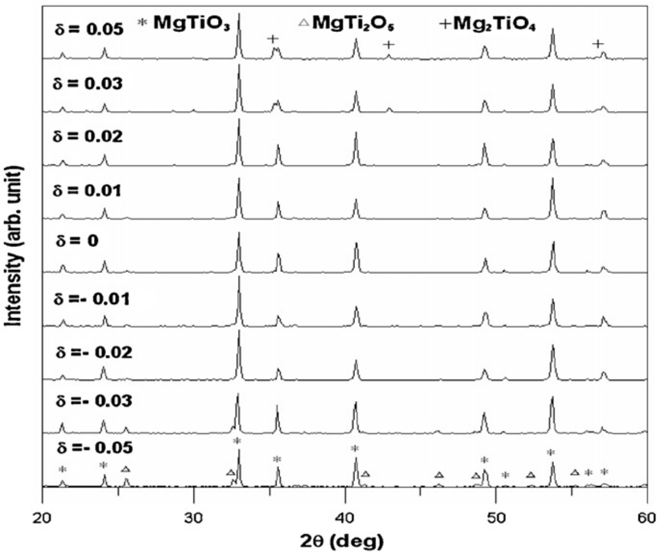

Fig. 2. XRD patterns of $Mg_{1+\delta}TiO_{3+\delta}$ ceramics sintered at 1400 °C for 4 h.

The powders were separately prepared according to the desired non-stoichiometry of $Mg_{1+\delta}TiO_{3+\delta}$ by using an electronic scale with an accuracy of three decimal, and ground in distilled water for 24 h in a ball mill with agate balls. The prepared powders were dried and calcined at 1100 °C for 4 h in air. The calcined reagent was ground into a fine powder for 12 h. A fine powder with 3 wt% of a 10% solution of polyvinyl alcohol (PVA 500, Showa, Japan) used as a binder was pressed into pellets 11 mm in diameter and 5 mm thick under a pressure of 200 MPa. The pellets were sintered at temperatures of 1310–1430 °C for 4 h in air. The heating and the cooling rates were both set at 10 °C/min.

The crystalline phases of the sintered ceramics were identified by XRD using Cu Kα (λ = 0.15406 nm) radiation with a Siemens D5000 diffractometer operated at 40 kV and 40 mA. The microstructural observations and analysis of the sintered surface were performed using a scanning electron microscope (SEM; Philips XL-40FEG, Eindhoven, The Netherlands) and an energy-dispersive X-ray spectrometer (EDS, Philips). The apparent densities of the sintered pellets were measured using the Archimedes method. The dielectric constant and the quality factor values at microwave frequencies were measured using the Hakki-Coleman dielectric resonator method [15,16]. A system composed of a HP8757D network analyzer and a HP8350B sweep oscillator was employed in the measurement. The technique used for the measurement of the temperature coefficient of resonant frequency (τ_f) was the same as that used for the quality factor measurement. The test cavity was placed over a thermostat. The temperature range was 25–80 °C. The τ_f (ppm/°C) was calculated by considering the change in resonant frequency (Δf):

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \tag{2}$$

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

3. Results and discussion

Fig. 2 illustrates the room-temperature X-ray diffraction (XRD) patterns recorded from $Mg_{1+\delta}TiO_{3+\delta}$ ceramics at 1400 °C for 4 h. The $MgTiO_3$ (ICDD #00-006-0494), as appeared in Fig. 2, was identified as the main crystalline phase for all specimens tested in the experiment. In addition to $MgTiO_3$, the crystalline phase of $MgTi_2O_5$ (ICDD #00-035-0792) also appeared at $\delta = -0.05$ and declined as the relative amount of Mg started to increase. However, the eradication of $MgTi_2O_5$ phase emerged and only $MgTiO_3$ was detected at $\delta = 0$ implying the forming of single $MgTiO_3$ phase. By increasing the δ value to 0.02, the specimen still retained a single phase and Mg_2TiO_4 (ICDD #00-025-1157) started to appear at $\delta = 0.03$ suggesting a possibility of the formation of a narrow homogeneity region $Mg_{1+\delta}TiO_{3+\delta}$ which existed at $0 \leq \delta \leq 0.02$. Further increase in the Mg content would lead to the increase of Mg_2TiO_4 phase. Moreover, no particular Si contamination was found from the XRD results.

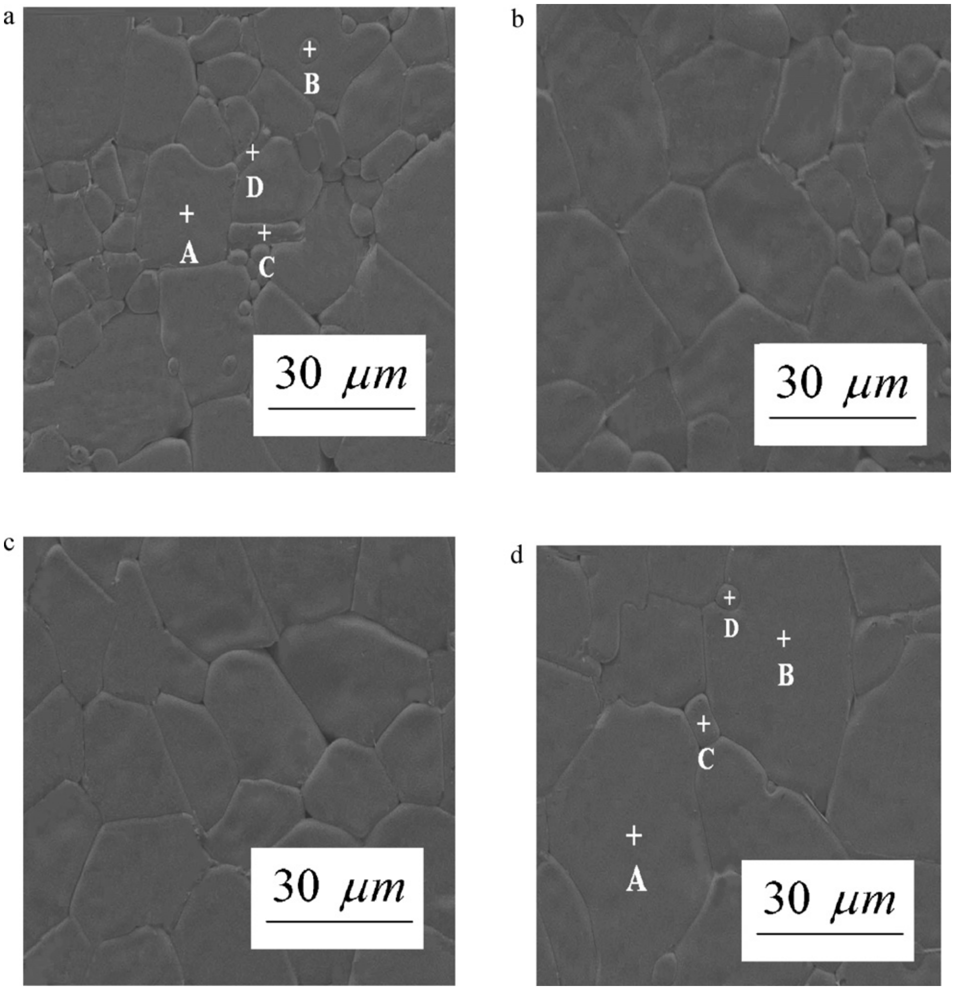

Fig. 3. SEM micrographs of $Mg_{1+\delta}TiO_{3+\delta}$ ceramics for δ = (a) −0.03, (b) 0, (c) 0.02, and (d) 0.03 sintered at 1400 °C for 4 h.

Table 2
EDS results of $Mg_{1+\delta}TiO_{3+\delta}$ ceramics corresponding to SEM photos in Fig. 3 for (a) $\delta = -0.03$ and (b) $\delta = 0.03$.

Spot	Atom (%)		
	MgK	TiO	OK
(a)			
A	20.12	19.57	60.31
B	19.86	19.12	61.02
C	12.37	24.55	63.08
D	12.98	24.26	62.76
(b)			
A	20.35	19.86	59.79
B	20.82	20.02	59.16
C	28.42	14.76	56.82
D	28.16	14.55	57.29

To identify each composition in the prepared ceramics, an EDS analysis was conducted for thermal-etched specimens using $Mg_{1+\delta}TiO_{3+\delta}$ sintered at 1400 °C for 4 h and the results are shown in Fig. 3 and Table 2. According to the quantitative analysis results, the large circular grains were $MgTiO_3$, rod-shaped grains were identified as $MgTi_2O_5$ ($\delta = -0.03$) phase and small circle-shaped grains indicated the Mg_2TiO_4 ($\delta = 0.03$) phase. These results were consistent with that from the XRD analysis. In addition, the average grain size of $MgTiO_3$ in the specimen with $\delta = 0.03$ is larger than that of specimen with $\delta = -0.03$ implying the increase of Mg content seems to promote the grain growth of the specimen. It may be because of the valence of Mg is smaller than that of Ti, which makes it easier to diffuse Mg^{2+} to TiO_2 to form $MgTiO_3$ rather than the other way around. In addition, the results of X-ray fluorescence analysis (XRF) of $Mg_{1+\delta}TiO_{3+\delta}$ ceramic were illustrated in Table 3 to confirm the actual degree of non-stoichiometry δ in the final ceramics. It also indicated a Si contamination due to the ball milling process with agate balls. However, the influence of the Si contamination on the dielectric properties of the specimens is likely limited because its weight percentage is rather small.

Table 4 shows the microwave dielectric properties of the non-stoichiometric $Mg_{1+\delta}TiO_{3+\delta}$ ceramic system sintered at 1400 °C for 4 h. Initially, the density apparently increased with increas-

Table 3
X-ray fluorescence analysis (XRF) of the $Mg_{1+\delta}TiO_{3+\delta}$ ceramics.

	MgO (wt%)	TiO_2 (wt%)	SiO_2 (wt%)	Mg:Ti (mole ratio)
$\delta = -0.03$	33.0157	66.8195	0.1648	0.979:1
$\delta = 0$	33.6456	66.1897	0.1647	1:1.007
$\delta = 0.02$	34.0218	65.7981	0.1801	1:1.025
$\delta = 0.03$	34.3982	65.4787	0.1231	1:1.041

Table 4
Microwave dielectric properties of the $Mg_{1+\delta}TiO_{3+\delta}$ ceramics sintered at 1400 °C for 4 h.

δ value	Apparent density (g/cm^3)	ε_r	$Q \times f$ (GHz)	τ_f (ppm/°C)
−0.05	3.70	17.8	68,200	−56
−0.03	3.72	17.9	10,5700	−52
−0.02	3.73	17.9	148,200	−52
−0.01	3.74	17.9	159,800	−50
0	3.75	17.9	167,200	−50
0.01	3.80	18.1	257,500	−50
0.02	3.84	18.3	357,600	−50
0.03	3.76	18.2	326,700	−49
0.05	3.72	18.1	263,900	−48

ing Mg content. After reaching its maximum at $\delta = 0.02$, it started to decrease which might be owing to the formation of Mg_2TiO_4 phase. The variation of ε_r is consistent with that of density. Since all the three phases $MgTiO_3$ ($\varepsilon_r \sim 17$, $Q \times f \sim 160{,}000$ GHz, $\tau_f \sim -50$ ppm/°C) [11], $MgTi_2O_5$ ($\varepsilon_r \sim 17.4$, $Q \times f \sim 47{,}000$ GHz, $\tau_f \sim -66$ ppm/°C) [17] and Mg_2TiO_4 ($\varepsilon_r \sim 14$, $Q \times f \sim 150{,}000$ GHz, $\tau_f \sim -50$ ppm/°C) [18] possess a similar ε_r, a negligible contamination of $MgTi_2O_5$ or Mg_2TiO_4 may not significantly deteriorate the ε_r of the $MgTiO_3$ suggesting the variation of ε_r is mainly controlled by the density. The τ_f also shows only a small variance within the range of −48 to −56 ppm/C for all compositions prepared in this experiment. However, a noticeably non-linear variation of the $Q \times f$ was observed. The $Q \times f$ value increased from 68,200 GHz at $\delta = -0.05$ to 167,200 GHz at $\delta = 0$ may be attributed to the elimination of $MgTi_2O_5$ phase, which has a low $Q \times f$ of ~47,000 GHz. As can be seen in Fig. 3, the grain size slightly increases with increasing δ because it is easier to diffuse Mg^{2+} to TiO_2 to form $MgTiO_3$ as described previously, which would result in a grain growth promotion. In addition, the microstructure still shows an inhomogeneous grain morphology at $\delta = -0.03$ and which can be improved by increasing the δ value to 0 and reaches a relatively uniform one at $\delta = 0.02$. It suggests the high $Q \times f$ may be also a result from the grain growth and the comparably uniform grain morphology of the specimen. Further increase in the δ will lead to the forming of Mg_2TiO_4 phase and the $Q \times f$ is then lowered. Notice that the $Q \times f$ of specimen at $\delta = 0$ is comparable with that proposed by Wakino [11]. With increasing Mg content, the $Q \times f$ of specimen would increase to a maximum of 357,600 GHz (at 10 GHz) at $\delta = 0.02$ and thereafter it decreased. It also shows a similar trend compared to that of density. Kim et al. [19] reported that the $Q \times f$ value of $MgTiO_3$ specimens could be improved to ~350,000–370,000 GHz with no second phase. The result is consistent with the maximum $Q \times f$ obtained in our study implying they may have a slight Mg-rich $MgTiO_3$ specimen. Since the specimen using $Mg_{1.02}TiO_{3.02}$ showed the highest $Q \times f$ value of 357,600 GHz, a more comprehensive investigation on the microwave dielectric properties of $Mg_{1.02}TiO_{3.02}$ was then conducted.

The room temperature X-ray diffraction (XRD) patterns recorded from the $Mg_{1.02}TiO_{3.02}$ ceramics sintered at different temperatures for 4 h are illustrated in Fig. 4. All specimens show a single $MgTiO_3$ phase with an ilmenite-type structure without the evidence of any additional second phase. In addition, no significant change was observed for specimens sintered at temperatures 1310–1430 °C. The lattice parameters was measured for $Mg_{1.02}TiO_{3.02}$ ceramics ($a = b = 5.0548(3)$ Å, $c = 13.8983(5)$ Å) in comparison with that of pure $MgTiO_3$ (a = b = 5.054Å, c = 13.898Å). The results illustrated that $Mg_{1.02}TiO_{3.02}$ ceramics would form a solid solution. Fig. 4 demonstrates the scanning electron microscopy (SEM) micrographs of the thermal-etched specimens using $Mg_{1.02}TiO_{3.02}$ ceramics sintered at different temperatures for 4 h. The result indicated that specimen sintered at 1310 °C, a porous microstructure was developed with numbers of pores and the grain size of the specimen was small, with an average grain size 2.27 μm. The increase of sintering temperature helped to promote the grain growth and a relative increase in the grain size was achieved for specimen sintered at 1370 °C. It was not until the temperature reached 1430 °C, that a rapid grain growth started to appear due to the over-sintering of the specimens and the grains are of relatively large size to an average of 29.11 μm. The grain size distributions are not very uneven compared to that prepared by a chemical route. However, a relatively uniform microstructure with low porosity was obtained for specimen sintered at 1400 °C. The well-developed microstructure has an average grain size of 27.27 μm, which is larger than that of stoichiometric $MgTiO_3$ ceramics [20] further confirming the promoted grain growth is due to the excess Mg content. Notice that the grain size analysis was accomplished by using the ASTM (American Society for Testing Material) E112 standard rules.

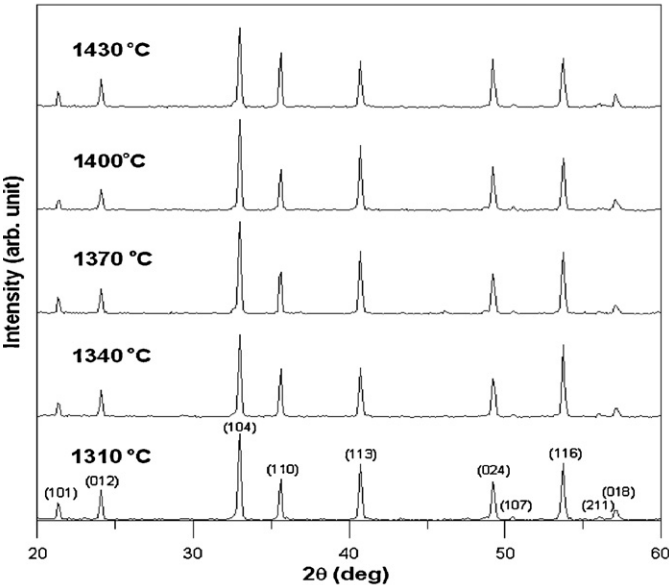

Fig. 4. XRD patterns of $Mg_{1.02}TiO_{3+\delta}$ ceramics sintered at various temperatures for 4 h.

Fig. 6 shows the apparent density and ε_r of $Mg_{1.02}TiO_{3.02}$ ceramics sintered at different temperatures for 4 h. With increasing temperature, the apparent density increased to a maximum value of 3.84 g/cm^3 at 1400 °C, and slightly declined thereafter. The decrease of density may be due to trapped porosity caused by the rapid grain growth as shown in Fig. 5 or abnormal grain growth. The variation of ε_r is consistent with that of the density. After reaching a maximum of 18.28 at 1400 °C, the ε_r value decreases. It is interesting to notice that the ε_r of $Mg_{1.02}TiO_{3.02}$ is higher than that of stoichiometric $MgTiO_3$. In addition, it only shows a small variance in the ε_r for specimens at temperatures from 1340 to 1430 °C implying that the influence of the temperature on the ε_r is almost negligible.

The $Q \times f$ and τ_f values of $Mg_{1.02}TiO_{3.02}$ ceramics sintered at different temperatures for 4 h are shown in Fig. 7. The $Q \times f$ of the specimen sintered at 1310 °C was relatively low due to the low density and porous microstructures, as shown in Figs. 5 and 6. By increasing the sintering temperature, the $Q \times f$ value increased to a maximum value of ~357,600 GHz (measured at 10 GHz) at 1400 °C and decreased thereafter. The $Q \times f$ value is an important index for dielectric ceramic applications at microwave and millimeter wave frequencies because high $Q \times f$ leads to low dielectric loss for microwave devices. Several factors contribute to dielectric loss at microwave frequencies, including density, porosity, second phases, and grain boundaries [21]. The variation of $Q \times f$ was also consis-

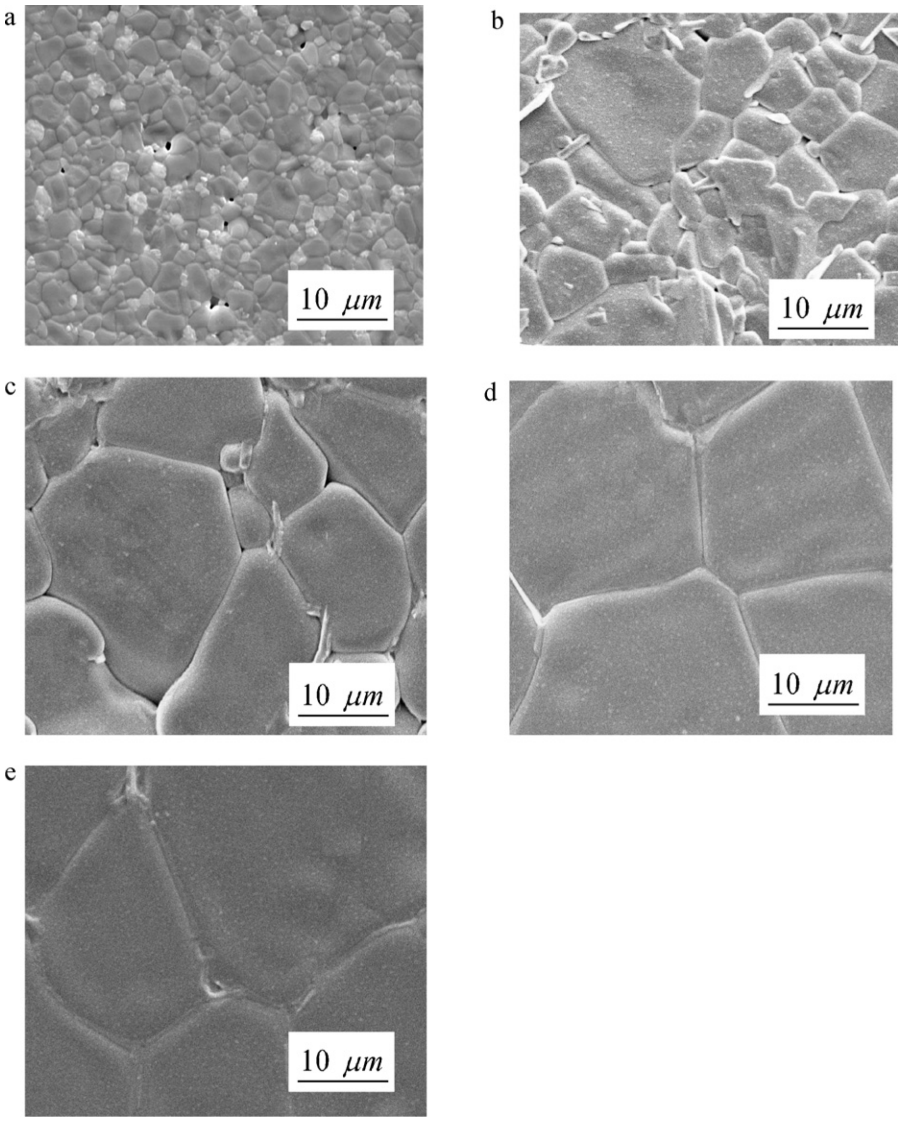

Fig. 5. SEM micrographs of $Mg_{1.02}TiO_{3.02}$ ceramics sintered at (a) 1310, (b) 1340, (c) 1370, (d) 1400, and (e) 1430 °C for 4 h.

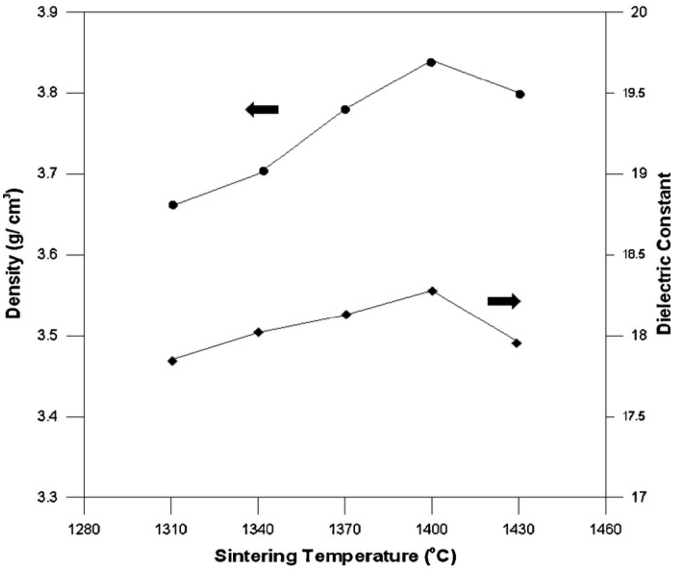

Fig. 6. Apparent density and dielectric constant of $Mg_{1.02}TiO_{3.02}$ ceramics as a function of sintering temperature.

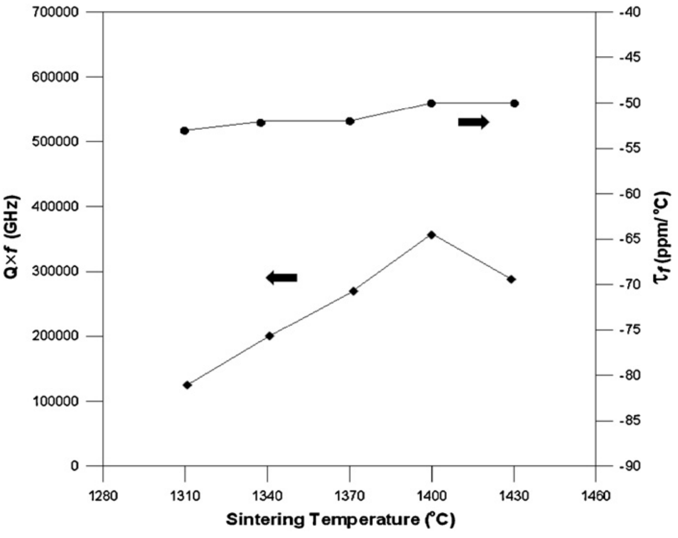

Fig. 7. $Q \times f$ and τ_f values of $Mg_{1.02}TiO_{3.02}$ ceramics as a function of sintering temperature.

tent with that of density suggesting the change of $Q \times f$ was mainly related to its corresponding density. Yang et al. also reported an improvement of the Q value of ceramics, which was explained by the increase in the grain size and relative density [22]. Because the grain boundary is a plane defect, it probably leads to a deterioration of the $Q \times f$ value of the specimen. Hence, the specimen with large grains is expected to have a high Q value because the grain growth decreases the grain boundary area. However, Alford and colleagues also indicated the grain boundaries have a very limited influence on the microwave dielectric loss and it was found that impurities and porosity were particularly deleterious to microwave loss in their recent studies [23]. Consequently, the improvement in the $Q \times f$ value of $Mg_{1.02}TiO_{3.02}$ might be attributed to the increase of density associated with a single $MgTiO_3$ phase, and a relatively uniform grain morphology as shown in Fig. 5. The temperature coefficient of resonant frequency (τ_f) is known to be governed by the composition, additives, and the second phase of the material. The τ_f almost retained constant throughout the entire temperature range in the experiment and showed only a small variance suggesting it is not sensitive to the temperature. At 1400 °C, a τ_f of −50 ppm/°C was obtained for $Mg_{1.02}TiO_{3.02}$ sintered for 4 h.

4. Conclusion

Low-loss, non-stoichiometric $Mg_{1+\delta}TiO_{3+\delta}$ $(-0.05 \le \delta \le 0.05)$ ceramics were prepared and their microwave dielectric properties and microstructure were investigated. Additional Mg from stoichiometry seemed to promote the grain growth of the specimen. A single $MgTiO_3$ phase could be achieved from the $Mg_{1+\delta}TiO_{3+\delta}$ within a narrow homogeneity region $0 \le \delta \le 0.02$. The $Q \times f$ varied non-linearly to a maximum of ~357,600 GHz at $\delta = 0.02$ and decreased thereafter. The high $Q \times f$s were associated with single $MgTiO_3$ phase. However, the ε_r and τ_f values were not sensitive to the composition and only showed a small variance in the experiment.

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