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Phase compositions and microwave dielectric properties of $MgTiO_3$-based ceramics obtained by reaction-sintering method

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Abstract
$MgTiO_3$-based microwave dielectric ceramics were prepared successfully by reaction sintering method. The X-ray diffraction patterns of the sintered samples revealed a major phase of $MgTiO_3$-based and $CaTiO_3$ phases, accompanied with Mg_2TiO_4 or $MgTi_2O_5$ determined by the sintering temperature and time. The microwave dielectric properties had a strong dependence of sintering condition due to the different phase compositions and the microstructure characteristics. The ceramics sintered at 1360 °C for 4 h exhibited good microwave dielectric properties: a dielectric constant of 20.3, a high quality factor of 48,723 GHz (at 9GHz), and a temperature coefficient of resonant frequency of −1.8 ppm/°C. The obtained results demonstrated that the reaction-sintering process is a simple and effective method to prepare the $MgTiO_3$-based ceramics for microwave applications.

Keywords Reaction sintering · Microwave dielectric properties · $MgTiO_3$?-based ceramic · Phase composition

1 Introduction

$MgTiO_3$ ceramics with ilmenite structure have attracted much attention due to their excellent microwave performances (ε_r ~17, $Q \times f$ ~350,000 GHz, and a negative τ_f of −50 ppm/°C) in the past three decades [1]. However, the large negative coefficient has been hampering the applications. Many researchers used the composition with positive coefficient, such as $CaTiO_3$ or $SrTiO_3$, to compensate the negative one of $MgTiO_3$ and obtained ceramics with near zero coefficients for microwave applications [2, 3]. In general, the preparation procedures of these composite systems are relatively complex. First, $MgTiO_3$ and $CaTiO_3$ or $SrTiO_3$ powders need to be synthesized separately using conventional solid reaction way or wet chemical methods. Then the powders are mixed, pressed and sintered. The repeated synthetic processes easily cause fluctuant microwave dielectric properties. Recently, Tang et al. investigated the effect of Mg:Ti ratio on the phase composition and microwave dielectric properties of $MgTiO_3$-based ceramics prepared by one synthetic process to simplify the procedure and obtained a ceramic with good microwave dielectric properties: $\varepsilon_r = 21.1$, $Q \times f = 79{,}915$GHz and $\tau_f = 1.2$ ppm/°C [4].

The reaction-sintering method has become an active research area in functional electronics applications which use improved microwave dielectric compounds, as well as the endeavor to reduce processing time by eliminating calcinations. This method has proved to produce ceramics with single phase such as $Ba_2Ti_9O_{20}$, $Li_2ZnTi_3O_8$, and $ZnZrNb_2O_8$ [5–7]. However, no reports referred to microwave dielectric ceramics with multi-phases, such as $MgTiO_3$-$CaTiO_3$ obtained by reaction-sintering. In this work, we investigated the phase compositions, microstructures and microwave dielectric properties of $MgTiO_3$ ceramics which were modified by $CaTiO_3$ and prepared by reaction-sintering method.

2 Experiments

According to our previous work, excess Mg was used to avoid the formation of the secondary phase such as $MgTi_2O_5$ for obtaining pure $MgTiO_3$ ceramic with excellent microwave dielectric properties [8]. Minor additives such as ZnO, Nb_2O_5 and MnO_2 could effectively improve the quality factor of titanate ceramics [9, 10]. Thus, highly pure MgO (99%),

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$CaCO_3$ (99.9%), TiO_2 (99.8%) were weighted according to the mole ratio of Mg: Ca: Ti = 0.97:0.05:1. Minor contents of ZnO (99%), Nb_2O_5 (99.5%) and $MnCO_3$ (98%) with a level of 0.1–0.4 wt% were used as modifiers. The above raw materials were mixed and ball milled with distilled water for 6 h and then dried. Next, the powders were mixed using PVA solutions as binder and pressed into pellets with a diameter of 12 mm and about 6 – 7 mm in thickness under a pressure of 150 MPa. The green pellets were sintered at 1300–1380 °C after de-binding.

Powder X-ray diffraction (XRD, D/max400, Rigaku, Japan) was used to confirm the phase structure of the samples. The microstructure characteristics were observed using scanning electron microscopy (FSEM, Ultra55, Carl zeiss NTS, Germany) with energy dispersive spectrometer. The bulk densities of the sintered specimens were measured by the liquid Archimedes method. The dielectric constant (ε_r) and the quality factor (Q_f) values were collected using the Hakki-Coleman dielectric resonator method with a vector-net-work analyzer (Agilent E5071C, U.S.A.) at around 9GHz. The temperature coefficient of resonant frequency (τ_f) was calculated by measuring the resonant frequency of $TE_{01\delta}$ mode at 20 °C and 80 °C.

3 Result and discussion

Figure 1 shows the X-ray diffraction patterns for the ceramics sintered at different temperatures for 4 h. The main crystalline phase belonged to the $MgTiO_3$-type (PDF#06–0494), accompanied with a minor phase of $CaTiO_3$ (PDF#22–0153). However, the other minor phases were different with different sintering temperatures. In the samples sintered below 1380 °C, Mg_2TiO_4 (PDF#25–1157) phase could be observed, while in the ceramic sintered at 1380 °C TiO_2 (PDF#21–1236) and $MgTi_2O_5$ (PDF#35–0796) were found. Furthermore, the diffraction peaks of $MgTiO_3$-type phase shifted to low angle when the sintering temperature increased from 1300 to 1340 °C, and then to high angle at 1360 and 1380 °C as shown in Fig. 1(b), which means that the crystal volume was first enlarged and then reduced. As we know, the cell volume of ceramics may be influenced by the sintering process, substitution, stress and other factors [11], although the actual reason for the lattice constant variation is still not clear. Since minor Zn^{2+} and Nb^{5+} were introduced in the preparation process, it could be proposed that the substitution of Zn^{2+} or Nb^{5+} for Mg^{2+} or Ti^{4+} in $MgTiO_3$ enlarged the crystal volume due to their larger ionic radius [12]. At 1360 and 1380 °C, the stress from grain boundary, abnormal grain growth or uniform grain size distribution might decrease the cell volume.

Figure 2 shows the scanning electronic micrographs of the ceramics sintered at 1340 (a), 1360 (b) and 1380 °C (c) and the energy dispersive spectra (d) of the area 1, 2, 3, and 4 in the SEM images. In the sample sintered at 1340 °C, there were some obvious pores and only one grain morphology with two different grain sizes. The EDS results of area 1 and 2 revealed that the grain exhibited a Mg:Ti ratio closing to 1. For the ceramics sintered at

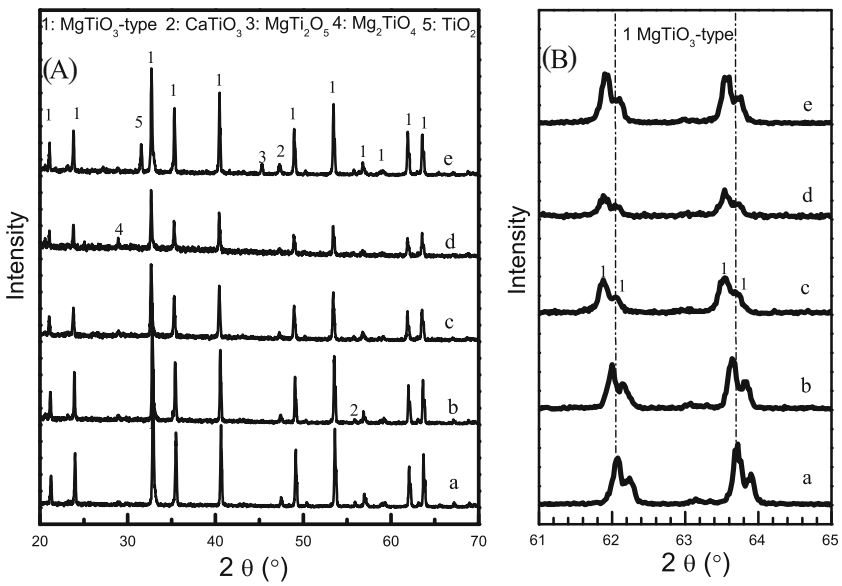

Fig. 1 (**a**): XRD patterns of $MgTiO_3$-based ceramics sintered at different temperatures (a: 1300 °C, b: 1320 °C, c: 1340 °C, d: 1360 °C and e: 1380 °C) for 4 h; (**b**): The enlargement of XRD patterns ar 2θ = 61–65 °

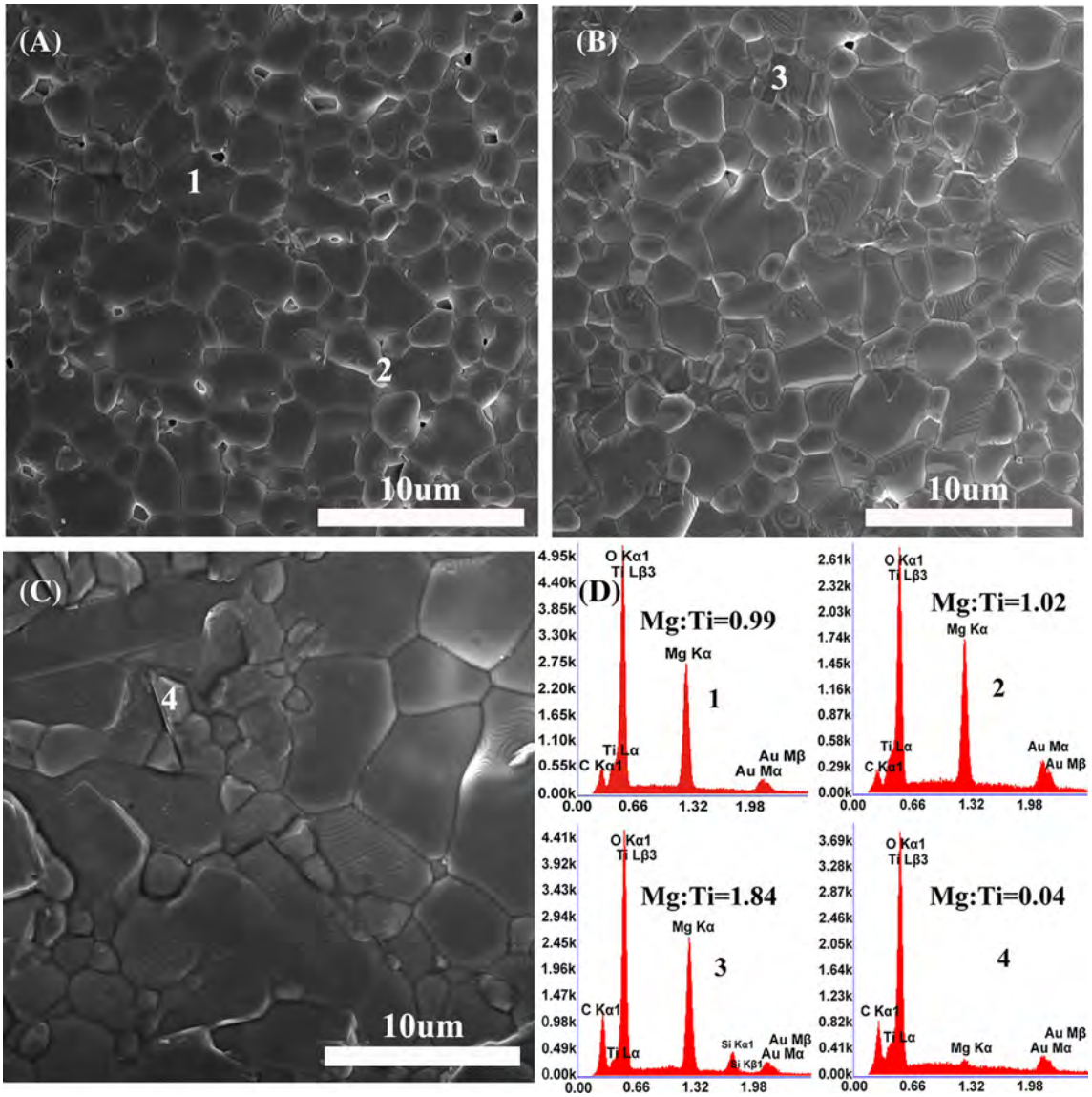

Fig. 2 SEM images of $MgTiO_3$-based ceramics sintered at 1340 (**a**), 1360 (**b**) and 1380 °C (**c**) for 4 h and EDS (**d**) of area 1, 2, 3 and 4 in (**a**, **b** and **c**)

1360 °C, there was nearly no pores and a similar grain morphology and grain size distribution to that at 1340 °C, accompanied with a dark strip grain (area 3 in Fig. 2(b)). The strip grain exhibited a Mg:Ti ratio of 1.84 shown in Fig. 2(d-3). At 1380 °C, abnormal grain growth appeared. Some grit-type grains (area 4 in Fig. 2(c)) were observed, which could be TiO_2 phase because Mg was almost not detected (Fig. 2(d-4)). Unfortunately, $CaTiO_3$ and $MgTi_2O_5$ phases were not identified.

The bulk densities and the microwave dielectric properties for the ceramics sintered at various temperatures are plotted in Fig. 3. When the sintering temperature increased from 1300 to 1360 °C, the density increased from 3.446 to 3.838 g/cm^3 sharply, due to the reduction of the porosity (Fig. 2) Further increasing temperature to 1380 °C, the value was lifted to 3.846 g/cm^3. The density is determined by the phase composition and the microstructure characteristics such as porosity. The densities of $MgTiO_3$, $MgTi_2O_5$, Mg_2TiO_4, $CaTiO_3$ rutile-TiO_2 were 3.895, 3.649, 3.546, 4.036 and 4.350 g/cm^3 respectively according to corresponding PDF card. Thus, the appearance of TiO_2 phase could contribute to the enhancement of density when the sintering temperature increased from 1360 to 1380 °C. The dielectric constant had a similar tendency to the bulk density (Fig. 3(a)) and increased from 11.5 to 20.3 when sintering temperature increased from 1300 to 1360 °C, which could be attributed to the reduction of porosity. Further

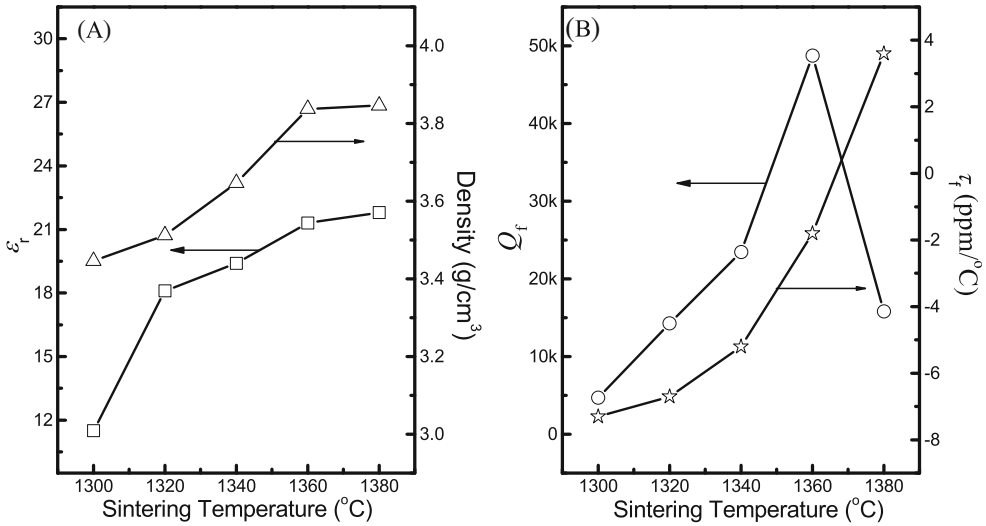

Fig. 3 (**a**) Dielectric constant (ε_r) and Density; (**b**) Quality factor (Q_f) and Temperature coefficient of resonant frequency (τ_f) of $MgTiO_3$-based ceramics sintered at different temperatures for 4 h. (Note: The arrow represents the corresponding performance.)

increasing temperature to 1380 °C, the dielectric constant increased slightly because of the relative high dielectric constants of TiO_2 (ε_r~100) [13] and $MgTi_2O_5$ (ε_r~17.4) [14].

The quality factor ($Q \times f$) was promoted from 4674 to 48,723 GHz with the sintering temperature increasing from 1300 to 1360 °C, and thereafter declined to 15,824 at 1380 °C, as shown in Fig. 3(b). This variation was similar to the changes in the density, the porosity and the phase compositions as well as the dielectric constant. At 1380 °C, the appearance of TiO_2 and $MgTi_2O_5$ increased the dielectric loss due to their low quality factors [13, 14]. Additionally, the abnormal grain growth was observed in the ceramics sintered at 1380 °C leading to the increase of the loss, because non-uniformity of grains would cause unexpected scattering of electromagnetic waves. The temperature coefficients of resonant frequency were in the range of −7.3 to −1.8 ppm/°C. However, at 1380 °C the value became positive since TiO_2 has a large positive τ_f (~ +420 ppm/°C) [13].

Based on the above observations, the study of sintering time dependent on the $MgTiO_3$-based ceramics was also carried out. Table 1 summarizes the performances of the ceramics sintered at 1360 °C for different times. The microwave dielectric properties were sensitive to the sintering time due to the different densities and phases compositions as well as above illustrations. Especially, the $Q \times f$ value decreased from 48,723 to 16,597 GHz significantly, which might be attributed to the formation of $MgTi_2O_5$ with relatively low quality factor [15], compared with the high quality factors (350,000 GHz for $MgTiO_3$ [1], 160,000 GHz for Mg_2TiO_4 [16]) and the abnormal grain growth from long soaking time at sintering temperature [17].

Shih investigated the difference in MgTiO3 ceramics prepared by conventional method and reaction sintering route [11], in which they attributed the low quality factor of the pure $MgTiO_3$ ceramic from the reaction sintering method than that from the conventional sintering to the non uniformity of grains, the existence of the microcracks when the calcinations was withdrawn, and the relatively small lattice volume from the reaction method. Thus, it could be proposed that the similar reasons might lead to the lower quality factor than that reported by Tang [4]. Future work should be considered and focused on the improvement of quality factor, when reaction sintering would be used.

Table 1 Summary of the $MgTiO_3$-based ceramics sintered at 1360 °C for different time

Sintering time (hour)	Phase composition (XRD results)	Density (g/cm^3)	Microwave dielectric properties		
			ε_r	Q_f	τ_f (ppm/°C)
2	$MgTiO_3$-type, $CaTiO_3$, Mg_2TiO_4	3.753	19.8	35,621	−4.7
4	$MgTiO_3$-type, $CaTiO_3$, Mg_2TiO_4	3.838	20.3	48,723	−1.8
6	$MgTiO_3$-type, $CaTiO_3$, Mg_2TiO_4, $MgTi_2O_5$	3.843	20.4	16,597	−2.6

4 Conclusions

In this work, we used reaction sintering method to obtain $MgTiO_3$-based ceramics with multi-phases. Sintering conditions dependent on the phase compositions, the microstructure characteristics and the microwave properties of $MgTi_3$-based ceramics were studied. Under the optimum sintering condition (1360 °C for 4 h in this study), the compact consisted of $MgTiO_3$-type phase, Mg_2TiO_4 and $CaTiO_3$ with a dielectric constant of 20.3, a quality factor of 48,723 GHz (at 9GHz) and a near zero temperature coefficient of −1.8 ppm/°C. The success of the reaction sintering process indicates its potential in microwave applications such as GPS antenna, to lower the preparation cost.

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