J Mater Sci (2009) 44:4993–4998
DOI 10.1007/s10853-009-3763-6

Dielectric properties and microstructure of TiO_2 modified $(ZnMg)TiO_3$ microwave ceramics with $CaO–B_2O_3–SiO_2$

Bo Li · Shuren Zhang · Ying Yuan · Xiaohua Zhou · Longcheng Xiang

Received: 30 March 2009 / Accepted: 18 July 2009 / Published online: 4 August 2009

Abstract The low-fired $(ZnMg)TiO_3–TiO_2$ (ZMT–TiO_2) microwave ceramics using low melting point $CaO–B_2O_3–SiO_2$ as sintering aids have been developed. The influences of Mg substituted fraction on the crystal structure and microwave properties of $(Zn_{1-x}Mg_x)TiO_3$ were investigated. The result reveals that the sufficient amount of Mg ($x \geq 0.3$) could inhibit the decomposition of $ZnTiO_3$ effectively, and form the single-phase $(ZnMg)TiO_3$ at higher sintering temperatures. Due to the compensating effect of rutile TiO_2 ($\tau_f = 450$ ppm/°C), the temperature coefficient of resonant frequency (τ_f) for $(Zn_{0.65}Mg_{0.35})TiO_3–0.15TiO_2$ with biphasic structure was adjusted to near zero value. Further, $CaO–B_2O_3–SiO_2$ addition could reduce the sintering temperature from 1150 to 950 °C, and significantly improve the sinterability and microwave properties of ZMT–TiO_2 ceramics, which is attributed to the formation of liquid phases during the sintering process observed by SEM. The $(Zn_{0.65}Mg_{0.35})TiO_3–0.15TiO_2$ dielectrics with 1 wt% $CaO–B_2O_3–SiO_2$ sintered at 950 °C exhibited the optimal microwave properties: $\varepsilon \approx 25$, $Q \times f \approx 47{,}000$ GHz, and $\tau_f \approx \pm 10$ ppm/°C.

Introduction

With the fast progress of microwave devices, the dielectric materials used for higher frequency regions have the increased demand. Many microwave ceramics with high quality factor (Q, $Q = 1/\tan\delta$) and relatively low dielectric constant (ε_r) as well as low temperature coefficient of resonant frequency (τ_f) have been extensively studied for such specific applications [1]. In addition, the development of low-temperature-cofired ceramics (LTCC) for microwave applications has received much attention, because of the design and functional benefits upon the miniaturization of multilayer devices with high electrical performance by using highly conductive internal electrode metals, such as Ag and Cu [1, 2].

Recently, zinc titanate ($ZnTiO_3$)-based systems have been developed and used as microwave materials for LTCC. Golovchanshi et al. [3] reported the microwave properties of hexagonal $ZnTiO_3$ ceramics prepared by sol–gel process: $\varepsilon_r \approx 19$, $Q \approx 3000$ (at 11 GHz), and $\tau_f \approx$ –55 ppm/°C. Kim et al. [4] studied the dielectric properties of the $ZnTiO_3–xTiO_2$ system, and also B_2O_3 was added to improve the sinterability. But the hexagonal $ZnTiO_3$ would decompose to TiO_2 and cubic Zn_2TiO_4 which has a rather low quality factor at above 945 °C [4, 5]. In order to overcome the above limitation in the sintering temperature, Kim et al. [6] investigated the low-fired $(Zn_{1-x}Mg_x)TiO_3$ microwave ceramics via semichemical synthesis route. In the recent papers [7–15], the glass phase additions, such as $ZnO–B_2O_3$, $B_2O_3–SiO_2$, $ZnO–B_2O_3–SiO_2$, on $ZnTiO_3$ or $(ZnMg)TiO_3$ materials have been carefully examined in terms of sinterability and dielectric properties. But until now, $CaO–B_2O_3–SiO_2$ (CBS) glass has not been reported in these systems.

In the present work, the low-fired $(ZnMg)TiO_3–TiO_2$ (ZMT–TiO_2) microwave ceramics using low melting point $CaO–B_2O_3–SiO_2$ as sintering aids have been developed. The influences of Mg-substituted fraction on the crystal structure and microwave properties of $(Zn_{1-x}Mg_x)TiO_3$ were investigated. Moreover, the rutile form of TiO_2 with good microwave properties ($\varepsilon_r \approx 100$, Q ≈ 16,000 at

B. Li (✉) · S. Zhang · Y. Yuan · X. Zhou · L. Xiang
State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, People's Republic of China
e-mail: lbuestc@163.com

3 GHz, $\tau_f \approx 450$ ppm/°C) [16] was used to compensate the negative τ_f of ZMT matrix. Further, CBS glass was added to lower the sintering temperature of ZMT–TiO_2, and the doping effect on the microstructure and microwave properties were also studied.

Experimental procedure

The samples were prepared by the conventional solid-state reaction method from individual reagent-grade oxide powders of 99.9% purity: ZnO, MgO, and rutile TiO_2. Firstly, the raw powders were weighed according to the compositions of $(Zn_{1-x}Mg_x)TiO_3$, and then milled for 24 h using ZrO_2 balls and ethanol. The obtained powders were calcined at 900 °C for 2 h in air. Secondly, the calcined powders mixed with the additions of TiO_2 (rutile) were ball-milled for 24 h in ethanol. Moreover, in order to lower the sintering temperature of $(ZnMg)TiO_3$-based ceramics, $CaO–B_2O_3–SiO_2$ glass nanopowders were added, which were synthesized by sol–gel process, see Ref. [17]. The mixed powders were ground with a suitable amount of polyvinyl alcohol as the binder and formed into disks (10 mm in diameter and 7 mm thickness) via uniaxial pressing at 15 MPa. Finally, these disks were sintered in the temperatures range from 950 to 1150 °C for 2 h in air, using the heating and cooling rates of 5 °C/min.

The crystalline structure of the fired specimens were identified by X-ray diffraction (XRD, Philips X' Pert Pro). The microstructure observations of the sintered surfaces were performed by means of scanning electron microcopy (SEM, Hitachi S-530) and energy dispersive X-ray analysis (EDX). The bulk sintered density of samples was measured using precision density balance (AND GF-300D) according to Archimedes method. The microwave dielectric properties of the sintered samples were evaluated in terms of the Hakki-Coleman method and using Agilent E8363A network analyzer in a resonant cavity. The temperature coefficients of resonant frequency (τ_f) were measured with changing temperatures from 20 to 80 °C, and calculated from the equation:

$$\tau_f = (f_{80} - f_{20})/(60 \times f_{20}) \times 10^6 (\mathrm{ppm}/^\circ\mathrm{C})$$

where f_{20} and f_{80} represent the resonant frequency at 20 and 80 °C, respectively.

Results and discussion

$(Zn_{1-x}Mg_x)TiO_3$ ceramics were calcined at 900 °C and sintered at 1150 °C, and then the crystal structure was analyzed. As shown in Fig. 1, the major phases of the sample with $x = 0.1$ are not $ZnTiO_3$ but unwanted TiO_2 and Zn_2TiO_4. For $x = 0.2$, typical diffraction lines of $ZnTiO_3$ are observed clearly accompanied by some TiO_2 and Zn_2TiO_4. And the desired hexagonal single-phase $(Zn_{1-x}Mg_x)TiO_3$ is formed completely when $x \geq 0.3$. Moreover, XRD peaks belonging to $MgTiO_3$ phase are not presented for all the samples, which indicates that Mg ions can easily substitute the zinc site and form the $(ZnMg)TiO_3$ solid solution. This is because $MgTiO_3$ has the same ilmenite structure as $ZnTiO_3$ and the smaller ionic radius of Mg^{2+} (0.66 Å) than that of Zn^{2+} (0.74 Å). In addition, although the formation of single $(ZnMg)TiO_3$ phase could be finished after the calcining stage, $(Zn_{1-x}Mg_x)TiO_3$ with lower contents of Mg ($x \leq 0.2$) would still decompose into TiO_2 and Zn_2TiO_4 at above 945 °C [4]. This phenomenon reveals that the sufficient amount of $MgTiO_3$ ($x \geq 0.3$) could inhibit the decomposition of $ZnTiO_3$ effectively, and form the single-phase $(ZnMg)TiO_3$ at a relatively higher sintering temperature. Kim et al. [6] also reported that the phase stability region of $(ZnMg)TiO_3$ increased to higher temperatures as the amount of Mg increased through the DSC examination.

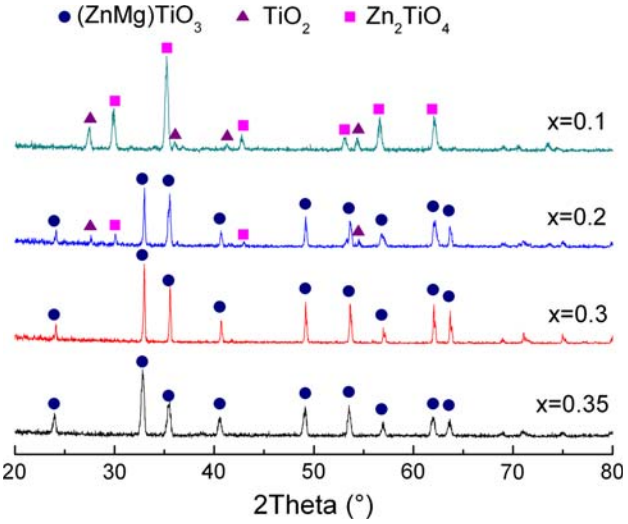

Fig. 1 XRD patterns of $(Zn_{1-x}Mg_x)TiO_3$ samples with different Mg content calcined at 900 °C and sintered at 1150 °C

Microwave properties of the sintered $(Zn_{1-x}Mg_x)TiO_3$ ceramics as a function of Mg content are illustrated in Fig. 2. It is found that with the increase of Mg content, the dielectric constant (ε_r) abruptly decreases at first, and then becomes stable when $x \geq 0.4$ ($\varepsilon_r \approx 19$). The relatively higher ε_r value for samples with $x \leq 0.2$ is attributed to the decomposition of $ZnTiO_3$ and the formation of high ε_r phase, rutile TiO_2 ($\varepsilon_r \approx 100$). And this results in an ε_r higher than that of pure $ZnTiO_3$. The gradual decrease of ε_r is due to the decrease of TiO_2 fraction and increase of $MgTiO_3$ ($\varepsilon_r \approx 17$) component in the ZMT solid solution.

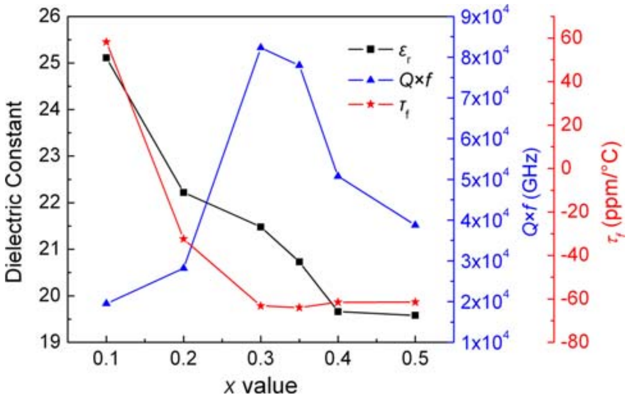

Fig. 2 Microwave properties tested at 10 GHz of $(Zn_{1-x}Mg_x)TiO_3$ specimens as a function of Mg content

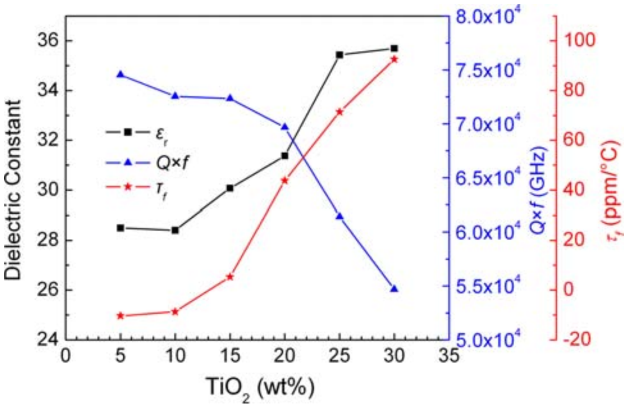

Fig. 3 Microwave properties (at 10 GHz) of TiO_2 modified $(Zn_{0.65}Mg_{0.35})TiO_3$ ceramics sintered at 1150 °C

The microwave material is often characterized by the $Q \times f$ value, which is the product of quality factor (Q) and resonant frequency (f). The $Q \times f$ values of specimens with $x \leq 0.2$ are lower than 30,000 GHz, because of high lossy Zn_2TiO_4 phase by decomposition of $ZnTiO_3$. In the range of $x = 0.3$–0.35, the $Q \times f$ values are about 75,000–85,000 GHz, where the specimens have hexagonal single phase and higher bulk density (4.48–4.61 g/cm^3). This result arose because the pure $MgTiO_3$ dielectric has a higher $Q \times f$ value ($\sim$160,000 GHz [18]) than $ZnTiO_3$ (33,000 GHz). However, high Mg content ($x \geq 0.4$) would cause the significant decrease of $Q \times f$ value, which seems to be due to the deterioration of sintering behavior, such as the decreased density, resulted from the high sintering temperature of $MgTiO_3$. Hsieh et al. [7] and Wang et al. [8] also found that the densification of $(Zn_{1-x}Mg_x)TiO_3$ ceramics extended to higher temperatures as the amount of Mg increased. Besides, the addition of Mg to $ZnTiO_3$ could decrease the density of the specimens, since the theoretical density of $MgTiO_3$ is 3.89 g/cm^3, while that of $ZnTiO_3$ is 5.16 g/cm^3. Therefore, the lower $Q \times f$ value of $(Zn_{1-x}Mg_x)TiO_3$ ($x \geq 0.4$) is attributed to the higher amount of magnesium.

The τ_f value of the sample with $x = 0.1$ has a large positive value ($\tau_f \approx 60$ ppm/°C), which is a result of the presence of TiO_2 ($\tau_f = 450$ ppm/°C). A near zero, τ_f value is obtained at around $x = 0.2$, but $Q \times f$ value is worse because of the low Q phase Zn_2TiO_4. When $x \geq 0.3$, the τ_f values are at around -60 to -65 ppm/°C and have no significant variation, because $ZnTiO_3$ ($\tau_f \approx -55$ ppm/°C) and $MgTiO_3$ ($\tau_f \approx -50$ ppm/°C) have close τ_f values. In general, $(Zn_{0.65}Mg_{0.35})TiO_3$ sintered at 1150 °C exhibit better microwave properties except a large negative τ_f (about -60 ppm/°C). Therefore, $(Zn_{0.65}Mg_{0.35})TiO_3$ was selected as base materials, TiO_2 ($\varepsilon = 100$, $\tau_f = 450$ ppm/°C) was used as modifier to compensate τ_f.

The microwave properties measured at 10 GHz of $(Zn_{0.65}Mg_{0.35})TiO_3$ ceramics are plotted in Fig. 3, as a function of the added TiO_2 content. As the amount of TiO_2 increases, the ε_r and τ_f values of the specimens increase gradually, which is attributed to high ε_r and τ_f values of TiO_2. The near zero τ_f value is attained between 10 and 15 wt% of TiO_2. However, with the increase of TiO_2, the value of $Q \times f$ decreases slowly at first, and then drops down dramatically above 20 wt% of TiO_2. As we know, the sintering temperature of TiO_2 is about 1450 °C and large amounts of TiO_2 would worsen the sintering behavior of $(Zn_{0.65}Mg_{0.35})TiO_3$ system. When TiO_2 is about 10–15 wt%, the sample exhibits excellent microwave properties: $\varepsilon = 28$–30, $Q \times f > 70{,}000$ (10 GHz), $\tau_f < \pm 10$ ppm/°C.

Figure 4 shows the XRD patterns of $(Zn_{0.65}Mg_{0.35})TiO_3$ with various TiO_2 additions sintered at 1150 °C. The major crystal phase is obviously hexagonal $(Zn_{0.65}Mg_{0.35})TiO_3$, while two secondary phases, i.e., TiO_2 and Mg_2TiO_5 are

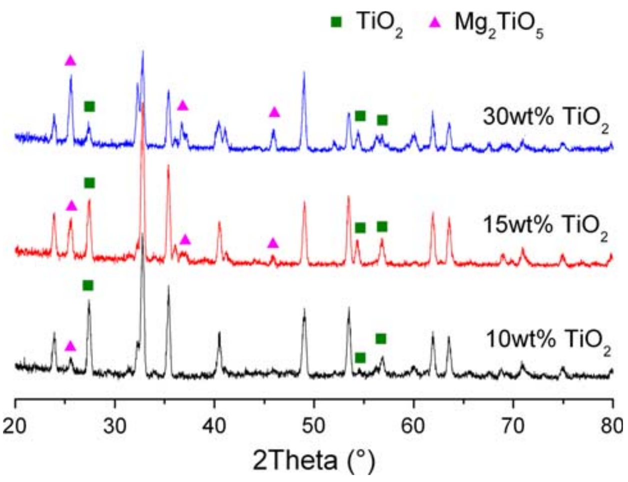

Fig. 4 XRD patterns of $(Zn_{0.65}Mg_{0.35})TiO_3$ with different amounts of TiO_2 fired at 1150 °C

also detected over the whole composition range. When TiO_2 addition is 10 wt%, the intensity of diffraction peaks for Mg_2TiO_5 phase is too weak to observe easily. But with increase of the doping concentration of TiO_2, the intensity for diffraction peaks of Mg_2TiO_5 becomes stronger notably, especially $TiO_2 = 30$ wt%. The presence of Mg_2TiO_5 originates from the chemical reaction at around 800 °C during sintering procedure.

$$MgTiO_3 + TiO_2 \rightarrow MgTi_2O_5$$

This indicates that redundant TiO_2 would react with $MgTiO_3$ to form the unexpected Mg_2TiO_5. However, Shin

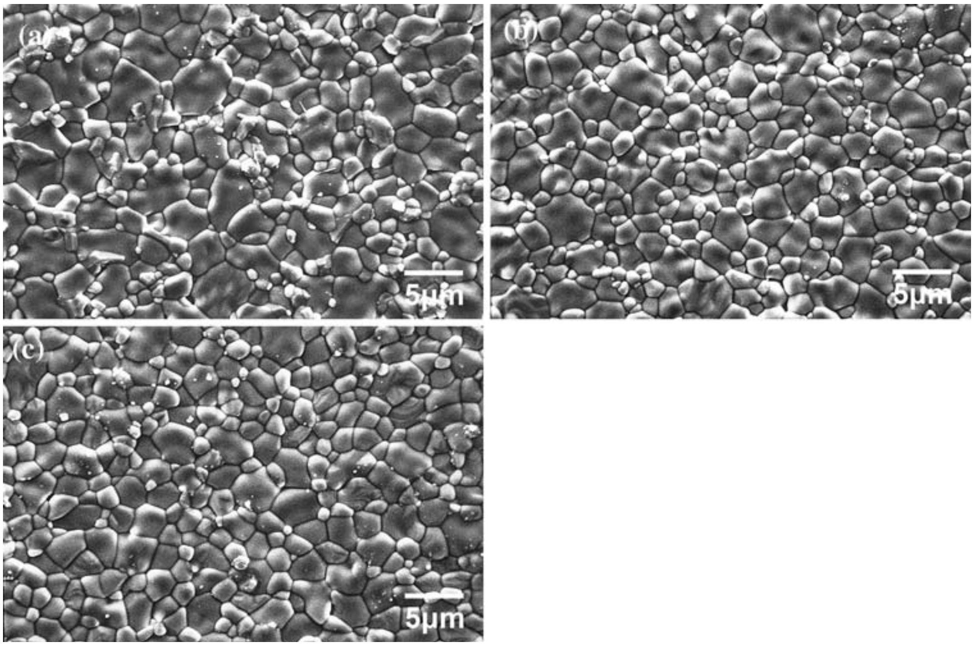

Fig. 5 SEM micrographs of $(Zn_{0.65}Mg_{0.35})TiO_3$ ceramics with different amounts of TiO_2 sintered at 1150 °C **a** 10 wt%, **b** 15 wt%, **c** 25 wt%

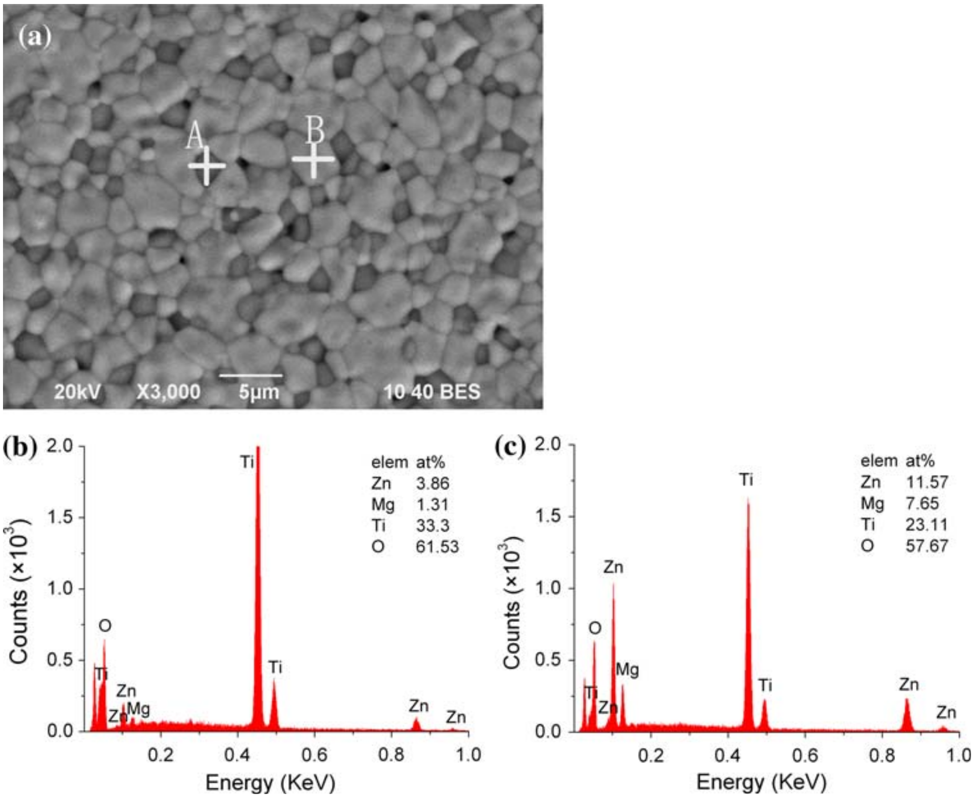

Fig. 6 SEM micrograph and EDX analysis of 15 wt% TiO_2 doped $(Zn_{0.65}Mg_{0.35})TiO_3$ microwave ceramic, **a** is the backscattered electron image; **b** and **c** are EDX spectrums for points A and B, respectively

et al. [19] reported that Mg_2TiO_5 exhibits good microwave dielectric properties ($\varepsilon_r = 17.4$, $\tau_f = -66$ ppm/°C, $Q \times f =$ 47,000 GHz), which is similar to $(Zn_{0.65}Mg_{0.35})TiO_3$ ceramics in our experiment. Thus, the presence of Mg_2TiO_5 cannot bring bad influence on the microwave properties of $(Zn_{0.65}Mg_{0.35})TiO_3$-based ceramics.

Figure 5 shows the evolution of microstructure of $(Zn_{0.65}Mg_{0.35})TiO_3$ doped with various amount of TiO_2 sintered at 1150 °C. It is observed that large grains together with fine grains coexist in these three samples. Subsequently, the two kinds of grains with different shapes were analyzed using EDS, and the corresponding results of SEM–EDS analysis are given in Fig. 6. From Fig. 6a, the small grains are relatively dark, compared with the large grains. In point A, Zn and Mg elements are hardly detected and Ti:O ≈ 1:2, so the small round grain is TiO_2. And in point B, (Zn + Mg):Ti:O ≈ 1:1:3, so the big rectangular grain is the $(Zn_{0.65}Mg_{0.35})TiO_3$ matrix phase. Moreover, the microstructures of the specimens look quite similar in Fig. 5. But as the added TiO_2 content increases, the $(Zn_{0.65}Mg_{0.35})TiO_3$ grains become smaller and the TiO_2 grains become bigger. The white spots distributed on the large grain randomly are considered to be the Mg_2TiO_5 minor phase, which is further supported by the results of XRD analysis in the previous study.

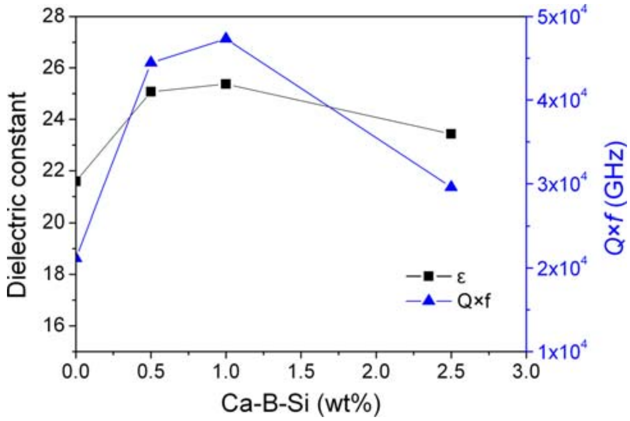

Fig. 7 Dielectric constant (ε) and $Q \times f$ value of $(Zn_{0.65}Mg_{0.35})TiO_3$–$TiO_2$ ceramics sintered at 950 °C as a function of CBS content

The variation of ε_r and $Q \times f$ values of $(Zn_{0.65}Mg_{0.35})TiO_3$–$0.15TiO_2$ ceramics sintered at 950 °C as a function of CBS content is depicted in Fig. 7. It is found that the ε_r and $Q \times f$ values increase significantly with increasing CBS content from 0 to 0.5 wt%, and reach the maximum value for the sample with 1 wt% CBS. Then the decrease in ε and $Q \times f$ values arise from the further increase in the CBS glass to 2.5 wt%. Thus, the sample with 1 wt% CBS glass exhibits attractive dielectric properties of $\varepsilon_r \approx 25$ and $Q \times f \approx$ 47,000 GHz.

In order to clarify the relationship between microstructures and microwave properties, the SEM micrographs of the samples sintered at 950 °C was investigated, and the results are shown in Fig. 8. With increasing the CBS content from 0.5 to 2.5 wt%, a remarkable change of grain shape for the samples is observed. It can be seen that the microstructure of the sample with 0.5 wt% CBS does not change significantly in comparison with CBS undoped one, while few glass phases occur in Fig. 8a. However, when the samples contain more than 1 wt% CBS glass, the grains of ZMT matrix are elongated and the grains of TiO_2 still remain round and small, as shown in Fig. 8b and c.

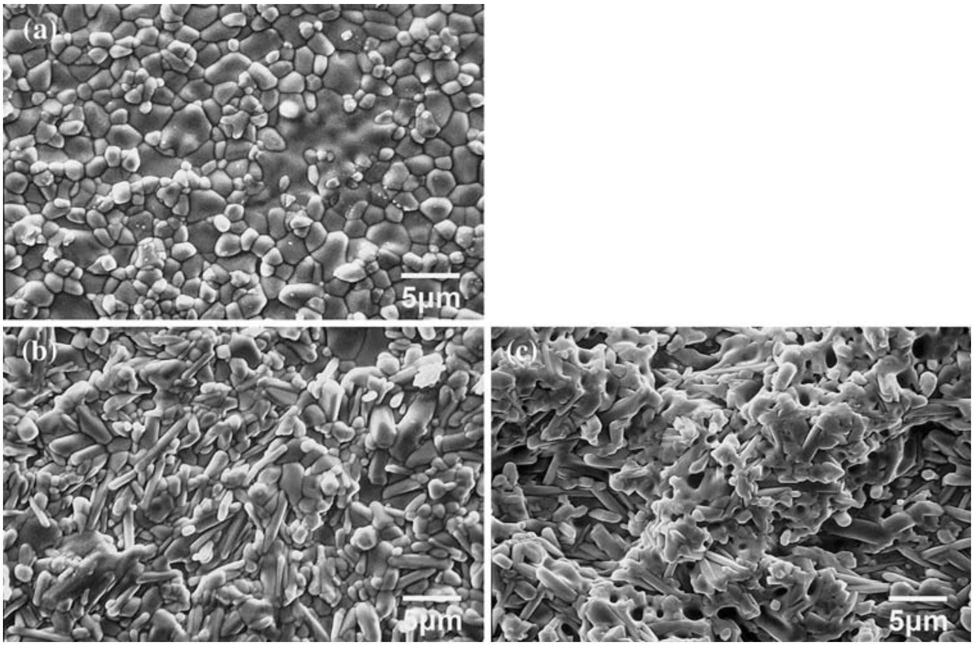

Fig. 8 SEM micrographs of $(Zn_{0.65}Mg_{0.35})TiO_3$–$0.15TiO_2$ ceramics with different amounts of CBS sintered at 950 °C **a** 0.5 wt%, **b** 1 wt%, **c** 2.5 wt%

Moreover, for the sample doped with 1 wt% CBS, the dense sintered ceramic body is obtained (4.23 g/cm^3) and a few glass phases distributed uniformly. But it is recognized that the deterioration in ε and $Q \times f$ value of the specimen with 2.5 wt% CBS is attributed to the presence of excess liquid phases as well as the rather porous microstructure (4.02 g/cm^3). Thus, a proper amount of CBS glass with low melting point (about 670 °C [17]) could form the liquid phase to lower the firing temperature and improving the densification during sintering, which could be the reason for achieving the good microwave performance.

Conclusions

The crystal phases and microwave properties of $(Zn_{1-x}Mg_x)TiO_3$ varied with the substituted Mg fraction. With the increase of Mg content, the decomposition of $ZnTiO_3$ was inhibited effectively, and the single-phase $(ZnMg)TiO_3$ was formed. The excellent microwave characteristics of ZMT ceramics were obtained at $x = 0.3$–0.35. Rutile TiO_2 with large τ_f value could compensate the negative τ_f of $(Zn_{0.65}Mg_{0.35})TiO_3$ system, and TiO_2 secondary phase coexists with $(ZnMg)TiO_3$ main phase in the ZMT–TiO_2 ceramics. TiO_2 (15 wt%) adjusted τ_f to near zero value. CaO–B_2O_3–SiO_2 with low melting point could reduce the sintering temperature from 1150 to 950 °C, and significantly improve the sinterability and microwave properties of ZMT–TiO_2 ceramics. The $(Zn_{0.65}Mg_{0.35})TiO_3$–$0.15TiO_2$ dielectrics with 1 wt% CaO–B_2O_3–SiO_2 sintered at 950 °C exhibited the optimal microwave properties: $\varepsilon \approx 25$, $Q \times f \approx 47{,}000$ GHz and $\tau_f \approx \pm 10$ ppm/°C.

References

1. Sebastian MT (2008) Dielectric materials for wireless communication. Elsevier
2. Sebastian MT, Jantunen H (2008) Int Mater Rev 53(2):57
3. Golovchanshi A, Kim HT, Kim YH (1998) J Korean Phys Soc 32(2):S1167
4. Kim HT, Kim SH, Nahm S, Byun JD (1999) J Am Ceram Soc 82(11):3043
5. Yamaguchi O, Morimi M, Kawabata H, Shimizu K (1987) J Am Ceram Soc 70(5):C97
6. Kim HT, Nahm S, Byun JD, Kim Y (1999) J Am Ceram Soc 82(12):3476
7. Hsieh M-L, Chen L-S, Wang S-M, Sun C-H, Weng M-H, Houng M-P, Fu S-L (2005) Jpn J Appl Phys 44(7A):5045
8. Wang Y-R, Wang S-F, Lin Y-M (2005) Ceram Int 31:905
9. Chaouchi A, d' Astorg S, Marinel S, Aliouat M (2007) Mater Chem Phys 103:106–111
10. Lee Y-C, Lee W-H (2005) Jpn J Appl Phys 44(4A):1838
11. Liu X, Gao F, Zhao L, Tian C (2007) J Alloys Compd 436:285
12. Chaouchi A, Aliouat M, Marinel S, d' Astorg S, Bourahla H (2007) Ceram Int 33:245
13. Lee Y-C, Lee W-H, Shiao F-T (2004) Jpn J Appl Phys 43(11A):7596
14. Zhang QL, Yang H, Zou JL, Wang HP (2005) Mater Lett 59:880
15. Chai Y-L, Chang Y-S, Hsiao Y-J, Lian Y-C (2008) Mater Res Bull 43:257
16. Templeton A, Wang X, Penn SJ, Webb SJ, Cohen LF, Alford NM (2000) J Am Ceram Soc 83(1):95
17. Zhou X, Li B, Zhang S, Ning H (2009) J Mater Sci: Mater Electron 20:262
18. Wakino K (1989) Ferroelectric 91:69
19. Shin H, Shin H-K, Jung HS, Cho S-Y, Hong KS (2005) Mater Res Bull 40(11):2021