Low temperature sintering and microwave dielectric properties of $(Zn_{0.65}Mg_{0.35})TiO_3$ ceramics with $BiVO_4$

Bo Li · Bin Tang · Shuren Zhang · Hongmei Jiang

Abstract The effects of $BiVO_4$ and $CaTiO_3$ additives on the microwave dielectric properties of $(Zn,Mg)TiO_3$ (ZMT) ceramics were investigated. $BiVO_4$ as a sintering agent could effectively lower the firing temperature of ZMT ceramics below 930 °C. From XRD analysis, the secondary phase formation occurred when $BiVO_4$ exceeding the solubility limit 2 wt% in ZMT matrix. SEM results indicated that due to the liquid phase sintering $BiVO_4$ significantly improved the grain growth and densification. With an increase of $BiVO_4$, the dielectric constant (ε_r) monotonously increased, but the quality factor (Qf) gradually decreased, and also the temperature coefficient of resonant frequency (τ_f) dramatically linear degraded. Besides, the addition of $CaTiO_3$ can adjust the τ_f value of this system to a near zero level. $(Zn_{0.65}Mg_{0.35})TiO_3$ ceramic codoped with 1.5 wt% $BiVO_4$ and 5 wt% $CaTiO_3$ additives sintered at 930 °C exhibited the good microwave dielectric properties of $\varepsilon_r = 23$, Qf = 16177 GHz, $\tau_f \approx 1.0$ ppm/°C.

Introduction

With the rapid growth of wireless communication industries, microwave devices with high performance and miniaturized size have become increasingly important. Dielectric materials having a high permittivity (ε_r), a high quality factor (Qf), and a near zero temperature coefficient of resonant frequency (τ_f) have been extensively studied for microwave devices. On the other hand, low temperature co-sintered ceramics

(LTCC) possessing good microwave dielectric properties has recently been widely investigated owing to the great potential for the application as multilayer microwave dielectric components. The sintering temperature of dielectrics for LTCC must be below 961 °C so as to co-fire with Ag internal electrode. However, conventional microwave ceramics usually require high firing temperature ranging from 1200 to 1500 °C to reach the high density and the high property. Hence, the development of LTCC material for microwave applications such as resonators, filters, and duplexers is urgently needed.

The results of the prior works showed that zinc titanates ($ZnO–TiO_2$, or $ZnTiO_3$) and their modified systems, with relatively low sintering temperatures and good dielectric properties, have been provided as suitable candidates for LTCC [1–4]. Nevertheless, there were some difficulties in the preparation of single-phase hexagonal $ZnTiO_3$, mainly because of the complicated phase transformation of $ZnTiO_3$ (specifically, the decomposition of $ZnTiO_3$ to Zn_2TiO_4 and rutile at above 945 °C) [5]. Therefore, $(Zn,Mg)TiO_3$ system has been developed since the substitution of Mg on Zn site can suppress the decomposition of $ZnTiO_3$ at the higher temperature [1, 2, 6]. To reduce the sintering temperature of $(Zn,Mg)TiO_3$, Kim et al. [6] prepared $(Zn,Mg)TiO_3$ using a semichemical synthetic route and a microbead milling technique. Besides, Kim et al. [5] found that the addition of B_2O_3 significantly enhanced the sinterability of $ZnTiO_3–TiO_2$ ceramics through the formation of a liquid phase. Recently, many studies reported the influences of glass frits (e.g. $ZnO–B_2O_3–SiO_2$ systems) and low melting point compounds (e.g. $B_2O_3–LiF$, $B_2O_3–V_2O_5$, Bi_2O_3) on the microstructure and microwave properties of $ZnTiO_3$ and $(Zn,Mg)TiO_3$ dielectrics [7–16].

In fact, $BiVO_4$, which acts as a typical flux, has been used for the liquid-phase sintering for other microwave

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dielectrics, such as $ZnNb_2O_6$, $BiNbO_4$, and $BiSbO_4$ [17–19]. However, the doping effects of $BiVO_4$ on the $ZnTiO_3$ and $(Zn,Mg)TiO_3$ were not reported yet. Thus, the sintering behavior, microstructures, and microwave dielectric properties of $BiVO_4$-doped $(Zn,Mg)TiO_3$ system were investigated in this work. Moreover, the addition of $CaTiO_3$ was employed to improve the microwave properties of this system and the modification effects were also researched.

Experiments

Powders of ZnO, $MgCO_3$, and TiO_2 (>99.5%, Xilong Chemical, China) were weighted according to the composition of $(Zn_{0.65}Mg_{0.35})TiO_3$. The powders were mixed in ethanol for 24 h in a balling mill, and then dried and calcined at 900 °C for 4 h. Bi_2O_3 and V_2O_5 (>99.5%, Xilong Chemical, China) were also ball milled for 24 h and calcined at 500 °C for 4 h to synthesize the sintering agent $BiVO_4$. $(Zn_{0.65}Mg_{0.35})TiO_3$ base materials were doped with x wt% $BiVO_4$ ($x = 1, 1.5, 2, 3, 5$) and y wt% $CaTiO_3$ ($y = 2, 4, 8$), re-milled with zirconia media in ethanol for 24 h. After drying and sieving, the powders were uniaxially pressed under a pressure of 15 MPa into disks of 10 mm in diameter and 7 mm in thickness. The disks were sintered in air at 890–950 °C for 2 h.
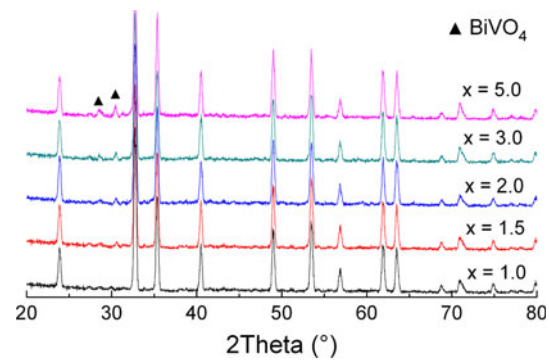
Crystalline phases of the sintered specimens were identified by an X-ray powder diffraction (XRD, Philips X' Pert Pro) using Cu K_α radiation ($\lambda = 1.54056$ Å). Microstructures of the specimens were studied using the scanning electron microscopy (SEM, Hitachi S-530). The densification behavior was evaluated by determining the bulk density using Archimedes technique. The microwave dielectric properties were measured by the Hakki–Coleman dielectric resonator method using Agilent E8363A network analyzer. The temperature coefficient of resonant frequency (τ_f) was also measured by the same method by changing temperature mainly from 20 to 80 °C and calculated from the following equation:

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

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

Results and discussion

Figure 1 shows the XRD patterns of $(Zn,Mg)TiO_3$ ceramics sintered at 930 °C with x wt% $BiVO_4$, which is used as the sintering agent. In our earlier work, hexagonal (rhombohedral) single-phase $(Zn_{0.65}Mg_{0.35})TiO_3$ powders were synthesized at 900 °C using the conventional solid-state reaction method [20]. Thus, all the sintered samples in the
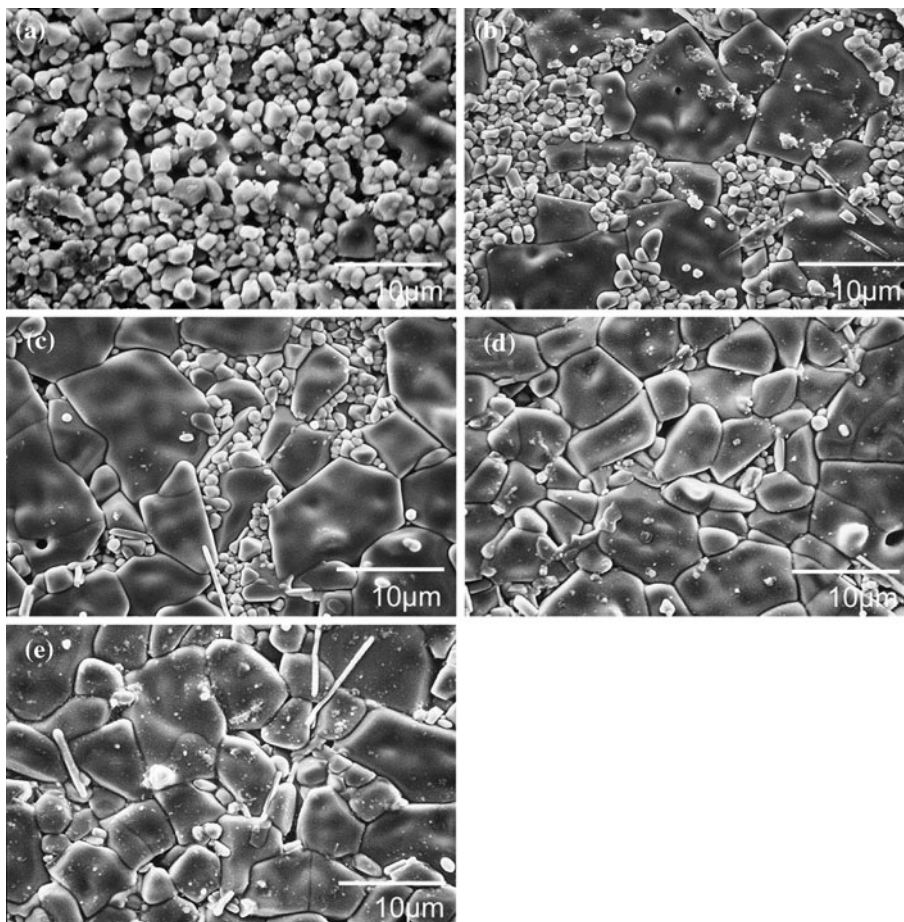

Fig. 1 XRD patterns of $(Zn,Mg)TiO_3$ ceramics with x wt% $BiVO_4$ additions sintered at 930 °C

present study show the $ZnTiO_3$ hexagonal phase as a main crystalline phase, as shown in Fig. 1. For ZMT ceramics with 1 and 1.5 wt% $BiVO_4$ additions, it is not found the extra peaks due to other second phases. But for ZMT ceramics with $BiVO_4 \geq 2$ wt%, it can be observed the major phase $ZnTiO_3$ along with an extra phase identified to be $BiVO_4$. And generally the relative peak intensities of the $BiVO_4$ phases increased with an increasing of $BiVO_4$ contents. It is known that the radius of the V^{5+} ion (0.59 Å) is similar to that of the Ti^{4+} (0.68 Å), and the Bi^{3+} (1.17 Å) is much larger than the Zn^{2+} (0.74 Å), according to Shannon's work [21]. So the small amount of V and Bi ions could be incorporated into the $ZnTiO_3$ crystal lattice, and form the $(Zn,Bi)(Ti,V)O_3$-type solid solutions. However, the extra $BiVO_4$, which cannot dissolve in the ZMT matrix, will precipitate as a secondary phase. It turns out from Fig. 1 that the solid solubility limit of $BiVO_4$ in $(Zn,Mg)TiO_3$ ceramics is lower than 2 wt%.
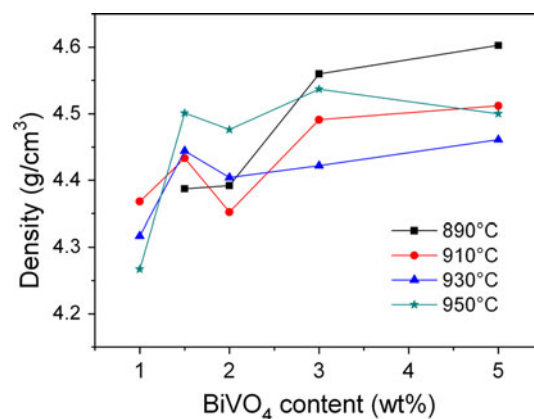
The SEM photographs of ZMT ceramics with x wt% $BiVO_4$ additions sintered at 930 °C are illustrated in Fig. 2. Although 1 wt% $BiVO_4$-doped specimen in Fig. 2a exhibits a uniform microstructure with fine grains (1–3 μm), the specimens containing ≥ 1.5 wt% of $BiVO_4$ phases show the abnormal grain-growth (>10 μm), and the grain size increases gradually for further increase of $BiVO_4$ content. This result indicates that the $BiVO_4$ addition has an obvious influence on the grain growth behavior of ZMT ceramics. As shown in Fig. 2b, c, the microstructure shows the mixture behavior for two kinds of grains. Besides, EDS analysis indicates that the concentration of $BiVO_4$ in the large grains especially near the grain boundary is higher than that in the small grains. It could be figured out that small amounts of Bi and V elements can be dissolved in ZMT phase, and promote the abnormal growth of ZMT grains. When $BiVO_4$ content further increased to 3 and 5 wt%, most of grains grow large and become uniform and dense (Fig. 2d, e). According to the results from XRD combined with EDS, the relative white matters randomly distributed in the ceramics are considered to be the secondary phase $BiVO_4$. Therefore,

Fig. 2 SEM photographs of ZMT ceramics doped with x wt% $BiVO_4$ additions sintered at 930 °C. **a** $x = 1$, **b** $x = 1.5$, **c** $x = 2$, **d** $x = 3$, **e** $x = 5$

this suggests that $BiVO_4$ formed the liquid phases during the sintering procedure, and excess fractions of $BiVO_4$ appeared at the grain boundary.

Figure 3 represents the bulk densities of ZMT ceramics as a function of $BiVO_4$ addition sintered at temperatures ranging from 890 to 950 °C. Since the theoretical density of $ZnTiO_3$ is 5.16 g/cm^3 and that of $MgTiO_3$ is 3.89 g/cm^3 [12], the calculated value of $(Zn_{0.65}Mg_{0.35})TiO_3$ is 4.716 g/cm^3. All the specimens reach to >90% of the theoretical density. As shown in Fig. 3, the lower density values reveal that 1 wt% $BiVO_4$ is not enough for completing the densification of ZMT ceramics in this lower temperature range. However, the densities of the specimens gradually increase with further increasing $BiVO_4$ addition in general. The dramatic enhancement of densities indicates that the addition of 1.5 wt% $BiVO_4$ could significantly improve the densification of ZMT ceramics. For 5 wt% $BiVO_4$-doped ZMT ceramics, the higher bulk density, 4.6 g/cm^3, could be reached when sample sintered at the lower temperature 890 °C, which indicates that a $BiVO_4$-related liquid phase is formed and the liquid phase can lower the sintering temperature effectively. In fact, Bi_2O_3–V_2O_5 composition with 1:1 mol ratio could form the eutectic phase which produced the liquid phase at temperatures lower than 650 °C. In
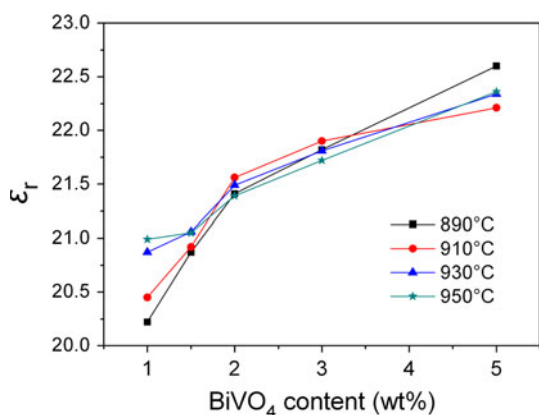

Fig. 3 Densities of ZMT ceramics as a function of $BiVO_4$ addition sintered at 890–950 °C
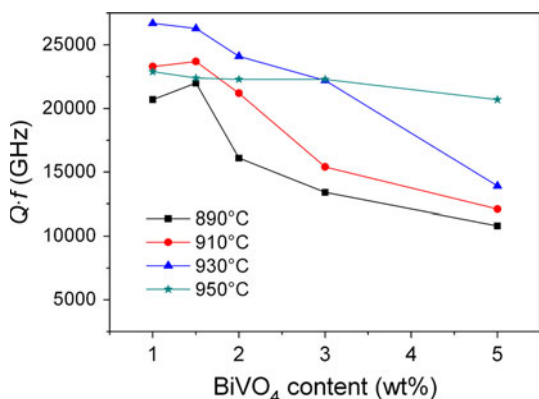
addition, the density of ceramic materials usually enhances with increasing the firing temperature. However, the decrement of density is clearly observed here as the firing temperature increases, which might be resulted from over-firing and/or the evaporation of Bi_2O_3 in these compounds. From the above results, it could be considered that the significant reduction in the sintering temperature of ZMT ceramics is possible owing to the $BiVO_4$ addition, and

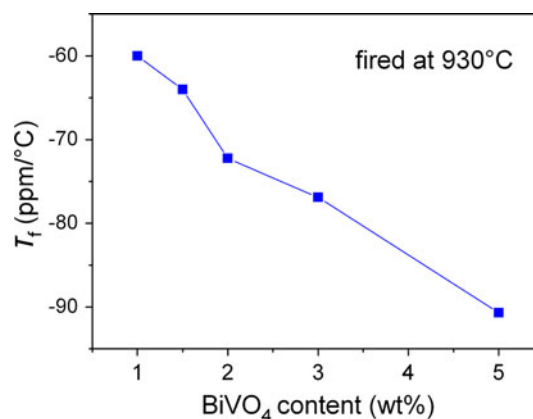meanwhile $BiVO_4$-doped ZMT dielectrics maintain the relatively high density.

Figures 4, 5, and 6 show the microwave dielectric properties of different amount of $BiVO_4$-doped $(ZnMg)TiO_3$ ceramics sintered at 890–950 °C. In the previous work, it indicated that the pure $BiVO_4$ sample exhibits microwave dielectric properties of $\varepsilon_r = 68$, $Qf = 8000$ GHz, $\tau_f \approx -243$ ppm/°C [17]. The dielectric constants vary as a function of $BiVO_4$ content, as shown in Fig. 4. The ε_r values of $BiVO_4$-doped ZMT samples monotonously increase with increasing $BiVO_4$ addition, which is surely due to the increment of the $BiVO_4$ inclusion in the ZMT matrix since $BiVO_4$ has a much higher ε_r value ($\varepsilon_r = 68$). In addition, the variation trend of ε_r values versus $BiVO_4$ addition is similar to the observed density behavior as shown in Fig. 3. The ε_r values are generally known to be affected by the morphology of the microwave ceramics, such as grain size and density. Therefore, it may be considered that on a basis of the density and microstructure observation, the increase of ε_r value is attributed to the liquid-phase densification with increasing amount of

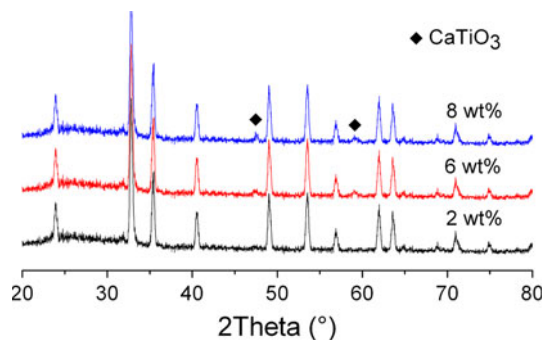**Fig. 6** Temperature coefficients of resonant frequency of ZMT ceramics with x wt% $BiVO_4$

$BiVO_4$ addition. Moreover, for 1–2 wt% $BiVO_4$-doped specimens, the ε_r value increases with sintering temperature; whereas for 3–5 wt% doped ones, the decrease of ε_r value is observed at higher temperature caused by overfiring. That is, the ε_r variation as a function of firing temperatures is also in accordance with the densification behavior.

The Qf values of x wt% $BiVO_4$-doped ZMT ceramics sintered at different temperature are presented in Fig. 5. It can be seen that the Qf values degrade with increasing the $BiVO_4$ content when the firing temperature is over 930 °C. This reduction of Qf values is obviously owing to the $BiVO_4$ with poor Qf value ($Qf = 8000$ GHz) according to the mixing effect. Nevertheless, the Qf values are maximized at 1.5 wt% of $BiVO_4$, and then degrade with increasing $BiVO_4$ addition also, when specimens are sintered at below 910 °C. On the other hand, the Qf values keep increasing as the sintering temperature increases from 890 to 930 °C. This is because the Qf values are independent of density or porosity for a relative density higher than 90% theoretical density of $(Zn_{0.65}Mg_{0.35})TiO_3$ (4.716 g/cm³). Moreover, the grains become large when the sintering temperature increases, which would result in lower dielectric loss. Because a large grain could lead to less grain boundary and less lattice mismatch. The maximum Qf value of 26300 GHz could be obtained at 930 °C for 1.5 wt% $BiVO_4$-doped ZMT ceramics.

Figure 6 plots the temperature coefficient of resonant frequency (τ_f) values of the $BiVO_4$ doped ceramics sintered at 930 °C as a function of the amount of $BiVO_4$ addition. It can be seen that the τ_f values at first slightly decrease from -60 to -64 ppm/°C with increasing $BiVO_4$ content from 1 to 1.5 wt% and then decrease steeply from -72.2 to -90.7 ppm/°C when the $BiVO_4$ content increase from 2 to 5 wt%. This gradually decrease in τ_f values as shown in Fig. 5 is ascribed to the addition of $BiVO_4$, since $BiVO_4$ possesses a much higher absolute value of negative τ_f

Fig. 4 Dielectric constants of ZMT ceramics sintered at 890–950 °C as a function of $BiVO_4$ content

Fig. 5 Qf values of ZMT ceramics sintered at 890–950 °C as a function of $BiVO_4$ additions
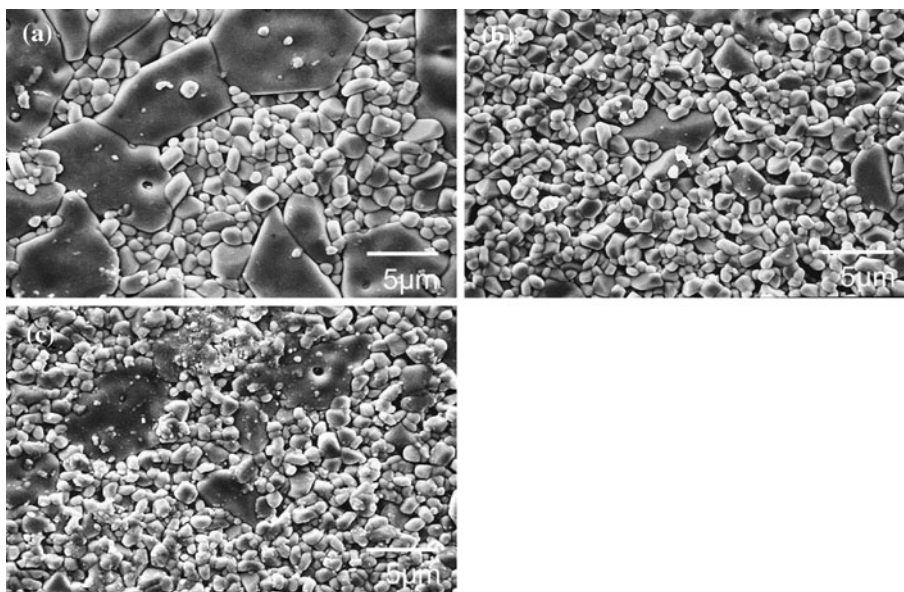
($\tau_f \approx -243$ ppm/°C [17]) compared with the pure $(Zn,Mg)TiO_3$. The presence of $BiVO_4$ phase in ZMT matrix was identified by the previous XRD in Fig. 1. According to the above analyses, it can be concluded that the small amount of $BiVO_4$ not only improved the microstructure and sintering behavior but also achieved the good microwave properties of this system. $(Zn_{0.65}Mg_{0.35})TiO_3$ ceramic with 1.5 wt% $BiVO_4$ sintered at 930 °C shows the dielectric properties of $\varepsilon_r = 21$, Qf = 26300 (15 GHz), $\tau_f \approx -64$ ppm/°C. But the τ_f has a much more negative value than we expected, and the further research for adjusting τ_f to zero is required.

The XRD patterns of ZMT ceramics with different amounts of $CaTiO_3$ additive are represented in Fig. 7. It is observed that only ≤2 wt% $CaTiO_3$-doped samples exhibit a single rhombohedral phase structure. However, the $CaTiO_3$ as a secondary phase is detected for specimens containing ≥6 wt% $CaTiO_3$. It is also shown that the $CaTiO_3$ peak intensities increase with increasing $CaTiO_3$

Fig. 7 XRD patterns of samples doped with different content of $CaTiO_3$ sintered at 930 °C

addition. It is believed from this result that the solid solubility of $CaTiO_3$ in ZMT ceramic is lower than 2 wt%. As we know, the ionic radius of Ca^{2+} (1.35 Å) is much larger than that of Zn^{2+} (0.74 Å), and $CaTiO_3$ different from $ZnTiO_3$ owns the cubic perovskite structure. Thus, only small amounts of Ca could be dissolved in the $(Zn,Mg)-TiO_3$ matrix and form the $(Zn,Mg,Ca)TiO_3$ solid solutions.

Figure 8 shows that the microstructure for the ZMT materials changes markedly with the $CaTiO_3$ additions. Although 2 wt% $CaTiO_3$-doped ZMT specimen in Fig. 8a shows the abnormal grain growth, the number of platy large grains reduces in comparison with the specimen without $CaTiO_3$ (Fig. 2a). Moreover, it can be seen from Fig. 8b,c that the specimens containing ≥6 wt% of $CaTiO_3$ almost have homogeneous microstructure except few exaggerated grains. That is to say, as the amounts of $CaTiO_3$ increase, the grain sizes of ZMT samples become small and uniform. This behavior seems to result in the $CaTiO_3$ addition enhancing the sintering temperature of this system, which means that $CaTiO_3$ with higher firing temperature could prevent the formation of liquid phase at such lower temperature 930 °C. Besides, the SEM-EDS analysis reveals that the bright grains randomly distributed in the ZMT matrix in Fig. 8c is the $CaTiO_3$ phase, which also demonstrated by the previous XRD.

It is well known that $CaTiO_3$ exhibits excellent microwave properties: $\varepsilon_r = 170$, Qf = 3600 (7 GHz), $\tau_f \approx 800$ ppm/°C. So different amount of $CaTiO_3$ compounds was incorporated into $BiVO_4$-doped $(Zn,Mg)TiO_3$ system in order to adjust the dielectric parameters, especially the τ_f value. Compared with ZMT ceramics, significantly improved microwave properties, i.e., $\varepsilon_r = 20.3$, Qf = 18400 GHz, $\tau_f \approx -6.5$ ppm/°C, are obtained for the
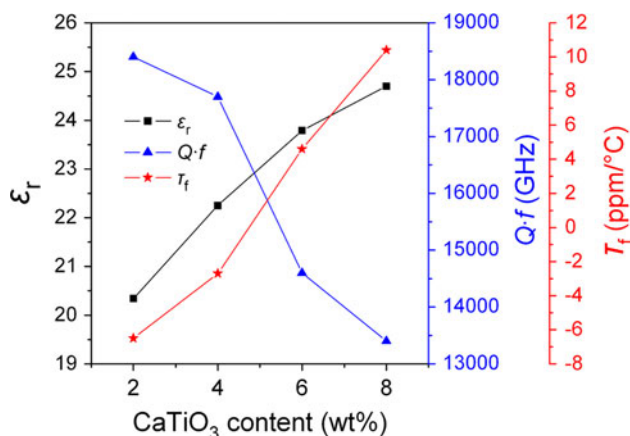

Fig. 8 SEM micrographs of ZMT ceramics doped with x wt% $CaTiO_3$ additions sintered at 930 °C. **a** $x = 2$, **b** $x = 6$, **c** $x = 8$

Fig. 9 Microwave dielectric properties of $CaTiO_3$ modified ZMT ceramics sintered at 930 °C

sample with 2 wt% $CaTiO_3$. As shown in Fig. 9, both ε_r and τ_f values of the specimens increased with increasing $CaTiO_3$ addition, which is attributed to the large value of ε_r and τ_f for $CaTiO_3$. Since the τ_f values gradually increase from -6.5 to 10.4 ppm/°C, the τ_f values of this system can be adjusted to a near zero by carefully controlling the content of $CaTiO_3$. In contrast, the value of Qf are decreased with increasing amount of $CaTiO_3$. This gradual degradation in Qf is attributable to the $CaTiO_3$ inclusion with relative lower Qf values and much higher firing temperature. Further, the latter reason for the decrease of Qf could be explained as follows. As the amount of $CaTiO_3$ increases, the sintering temperature of $CaTiO_3$-doped system would be enhanced and the densification behavior could be deteriorated. Eventually, $(Zn_{0.65}Mg_{0.35})TiO_3$ ceramic codoped with 1.5 wt% $BiVO_4$ and 5 wt% $CaTiO_3$ additives sintered at 930 °C shows the good microwave dielectric properties: $\varepsilon_r = 23.0$, Qf = 16177 GHz, $\tau_f \approx 1.0$ ppm/°C.

Conclusion

The addition of $BiVO_4$ as a sintering agent to $(Zn,Mg)TiO_3$ ceramics could be lower the sintering temperature below 950 °C. With increasing the $BiVO_4$ additive, low-fired ZMT ceramics exhibit a monotonous increase in dielectric constant (ε_r), a gradual decrease in the quality factor (Qf), and a dramatically linear degradation in the temperature coefficient of resonant frequency (τ_f). These can be surely attributed to the increment of the $BiVO_4$ inclusion in the ZMT matrix, since $BiVO_4$ has a much higher ε_r, lower Qf and negative τ_f value. Besides, small amounts of $BiVO_4$ could dissolve into ZMT matrix, and the extra $BiVO_4$ beyond the solubility limit 2 wt% will precipitate as a secondary phase. $BiVO_4$ could promote the grain growth and improve the densification of ZMT ceramics significantly. 1.5 wt% $BiVO_4$-doped $(Zn_{0.65}Mg_{0.35})TiO_3$ ceramics sintered at 930 °C showed the dielectric properties of $\varepsilon_r = 21$, Qf = 26300 (15 GHz), $\tau_f \approx -64$ ppm/°C.

The ε_r and τ_f values of the specimens increased with increasing $CaTiO_3$ addition due to the $CaTiO_3$ with large ε_r and τ_f value. Therefore, the τ_f values of this system can be adjusted a near zero by carefully controlling the content of $CaTiO_3$ compounds. Moreover, the solid solubility of $CaTiO_3$ in ZMT system is lower than 2 wt%, and $CaTiO_3$ with higher firing temperature could prevent the formation of liquid phase as well as the abnormal grain growth. In this work, $(Zn_{0.65}Mg_{0.35})TiO_3$ ceramic codoped with 1.5 wt% $BiVO_4$ and 5 wt% $CaTiO_3$ additives sintered at 930 °C exhibited the good microwave dielectric properties: $\varepsilon_r = 23$, Qf = 16177 GHz, $\tau_f \approx 1.0$ ppm/°C.

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