LOW-TEMPERATURE SINTERED $(ZnMg)_2SiO_4$ MICROWAVE CERAMICS WITH TiO_2 ADDITION AND CALCIUM BOROSILICATE GLASS

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The low-temperature sintered $(ZnMg)_2SiO_4$–TiO_2 microwave ceramic using CaO–B_2O_3–SiO_2 (CBS) as a sintering aid has been developed. Microwave properties of $(Zn_{1-x}Mg_x)_2SiO_4$ base materials via sol-gel method were highly dependent on the Mg-substituted content. Further, effects of CBS and TiO_2 additives on the crystal phases, microstructures and microwave characteristics of $(ZnMg)_2SiO_4$ (ZMS) ceramics were investigated. The results indicated that CBS glass could lower the firing temperature of ZMS dielectrics effectively from 1170 to 950°C due to the liquid-phase effect, and significantly improve the sintering behavior and microwave properties of ZMS ceramics. Moreover, ZMS–TiO_2 ceramics showed the biphasic structure and the abnormal grain growth was suppressed by the pinning effect of second phase TiO_2. Proper amount of TiO_2 could tune the large negative temperature coefficient of resonant frequency (τ_f) of ZMS system to a near zero value. $(Zn_{0.8}Mg_{0.2})_2SiO_4$ codoped with 10 wt.% TiO_2 and 3 wt.% CBS sintered at 950°C exhibits the dense microstructure and excellent microwave properties: ε_r = 9.5, $Q{\cdot}f$ = 16 600 GHz and τ_f = −9.6 ppm/°C.

INTRODUCTION

The rapid progress in mobile and satellite communication systems have increased the demand for the development of dielectric materials for higher band microwave devices. A high quality factor ($Q{\cdot}f$), a low permittivity (ε_r) and a stable temperature coefficient of resonant frequency (τ_f) is necessary for these materials. Thus, a number of such material systems including Zn_2SiO_4, Al_2O_3, Mg_2SiO_4, $CaWO_4$ and $Mg_4Nb_2O_9$ have been developed [1-5]. Moreover, low temperature co-sintered ceramics (LTCC) for multilayer devices have been extensively investigated in order to miniaturize microwave components. Silver with high conductivity and low cost has been widely used as internal electrode metals. However, because of the low melting point of silver, microwave dielectrics cofired with Ag electrode require the sintering temperature lower than 961°C. However, the sintering temperature of the above materials is high and needs to be decreased before they can be considered for use as LTCC devices.

Guo et al. [1] reported that Zn_2SiO_4 ceramics prepared by solid-state method sintered at 1280 ~ 1340°C exhibited millimeter-wave dielectric properties: ε_r = 6.6, $Q{\cdot}f$ = 219 000 GHz, τ_f = -61 ppm/°C. And 11 wt.% TiO_2 modified Zn_2SiO_4 ceramics sintered at 1250°C showed a nearly zero τ_f value of 1.0 ppm/°C and ε_r of 9.3, $Q{\cdot}f$ of 113 000 GHz. Nguyen et al. [6] studied the effect of Zn/Si ratio on the microstructure and microwave properties of $Zn_{2-x}SiO_{4-x}$ ceramics, and found that a low $Q{\cdot}f$ value of Zn_2SiO_4 was possibly due to the formation of ZnO second phase and $Zn_{1.8}SiO_{3.8}$ sintered at 1 300°C showed improved microwave properties of ε_r = 6.6, $Q{\cdot}f$ = 147 000 GHz, and τ_f = -22 ppm/°C. Besides, Song et al [7] improved the $Q{\cdot}f$ value of Zn_2SiO_4 ceramics by Mg^{2+} substituting for Zn^{2+}, and $(Zn_{0.6}Mg_{0.4})Si_2O_4$ ceramics achieved the dielectric properties in the temperature range from 1200 to 1500°C: ε_r = 6.6, $Q{\cdot}f$ = 95650 GHz and τ_f = -60 ppm/°C. Thus, the high sintering temperature and large negative τ_f value of Zn_2SiO_4-based systems restricts their use as microwave materials for LTCC. Zou et al [8] reported that ZnO−0.6SiO_2 ceramics with 5 wt.% Li_2CO_3 - 4 wt.% Bi_2O_3 addition can be sintered at a low temperature 910°C and showed ε_r of 6.65, $Q{\cdot}f$ of 33 000 GHz, and τ_f value of -70 ppm/°C. Recently, Kim et al. [9] chose B_2O_3 to decrease the firing temperature of $Zn_{1.8}SiO_{3.8}$ ceramics and the specimen containing 20 mol.% B_2O_3 sintered at 900°C had good microwave properties of ε_r = 5.7, $Q{\cdot}f$ = 53000 GHz, and τ_f = = -16 ppm/°C. In our previous study, the sintering temperature of $(Zn_{1-x}Mg_x)_2SiO_4$ ceramics could be effectively reduced to 1170°C by using the sol-gel process [10].

In this work, $CaO–B_2O_3–SiO_2$ (CBS) glass [11] was used as a sintering aid to low the firing temperature of $(ZnMg)_2SiO_4$ ceramics, which has not been reported until now. TiO_2 with large positive τ_f value of 450 ppm/°C [12] was added to this system in order to adjust the τ_f value. The influences of CBS glass and TiO_2 on the microstructure and microwave dielectric properties of $(ZnMg)_2SiO_4$ ceramics were investigated.

EXPERIMENTAL METHODS

Specimen preparation

Using the method of sol-gel synthesis, $(Zn_{1-x}Mg_x)_2SiO_4$ (x = 0.1, 0.2, 0.3, 0.4) was prepared from reagent grade ZnO, $MgCO_3$ and $(C_2H_5)_4SiO_4$ (see Ref. [10]) and calcined at 850°C. Meanwhile, $CaO–B_2O_3–SiO_2$ (CBS) glass was also prepared by sol-gel method and calcined at 550°C [11]. Then, 1 ~ 4 wt.% CBS and/or 6 ~ 12wt.% TiO_2 were added into the $(ZnMg)_2SiO_4$ base materials, and then ball milled in ethanol for 24 h with ZrO_2 balls. After drying and sieving, the powders with 10 wt.% PVA were granulated and pressed into disks with 10 mm diameter and 7 mm thickness under a pressure of 15 MPa. Finally, the disks were sintered at 930~1000°C for 2 h in air.

Characterization

The crystal phases and microstructures of the sintered ceramics were examined by X-ray diffraction analysis (XRD, Philips X'Pert-MPD) and scanning electron microscopy (SEM, Jeol JSM-6490LV), respectively. The microwave dielectric characteristics the samples were measured by the Hakki-Coleman dielectric resonator method using an Agilent E8363A network analyzer. The dielectric properties were calculated from the frequency of the TE_{011} resonant mode. The temperature coefficient of resonant frequency (τ_f) was measured at a temperature in the range from 25 to 75°C and calculated by the following equation:

$$\tau_f(\text{ppm/°C}) = (f_{75} - f_{25})/(50{\cdot}f_{25}) \times 10^6 \qquad (1)$$

where f_{25} and f_{75} is the resonant frequency at 25 and 75°C, respectively.

RESULTS AND DISCUSSION

The microwave dielectric properties of $(Zn_{1-x}Mg_x)_2SiO_4$ ceramics sintered at 1170°C were investigated, and the data as a function of Mg-substituted content are drawn in Figure 1. It is found that the variation of dielectric constant (ε_r) and $Q{\cdot}f$ values of samples exhibit the similar trend. As the amount of Mg increases, the value of ε_r and $Q{\cdot}f$ increase abruptly at first and reach the maximum at x = 0.2, yet then decrease dramatically. In fact, the dielectric characteristics are usually affected by the sintering behavior and microstructures. Moreover, Song et al [7] suggested that it is difficult for Zn_2SiO_4 ceramics to obtain a dense microstructure and its sintering range is very narrow. By appropriate Mg^{2+} substituting for Zn^{2+}, the sintering range is widened and the sintering temperature of Zn_2SiO_4 ceramics can be lowered from 1400 to 1250°C. Besides, the τ_f values change slightly (-63 ~ -58 ppm/°C) versus Mg content. This is attributed to the nearly same τ_f value of Zn_2SiO_4 and Mg_2SiO_4 phases. So $(Zn_{0.8}Mg_{0.2})_2SiO_4$ ceramics exhibits excellent microwave properties: ε_r = 6.3, $Q{\cdot}f$ = 189 800 GHz and τ_f = -63 ppm/°C.

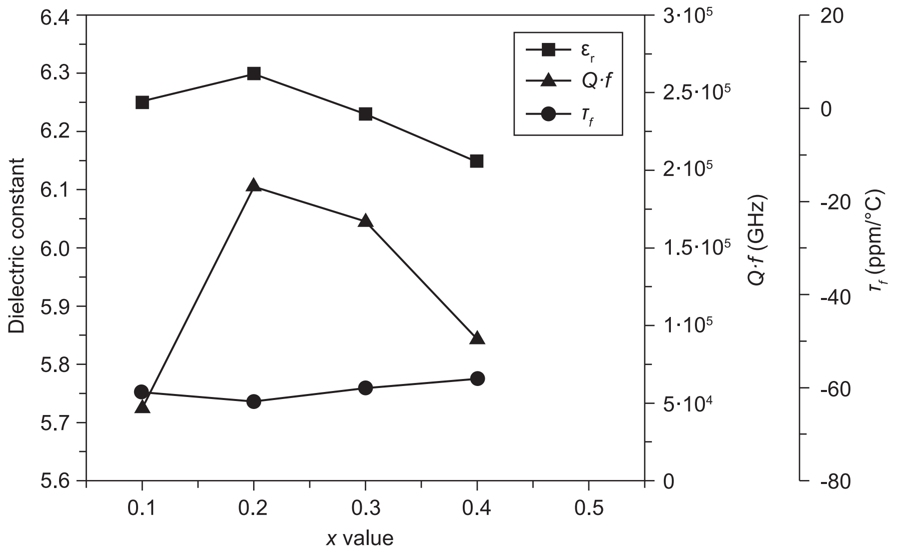


Figure 1. Microwave dielectric properties of $(Zn_{1-x}Mg_x)_2SiO_4$ ceramics sintered at 1170°C.

SEM micrographs of the ZMS ceramics sintered at 950°C doped with *x* wt.% CBS are shown in Figure 2. For the sample with 1 wt.% CBS, the microstructure of the sintered ceramic is porous, while the grains are small. With increasing the CBS content, the grain size of the specimens obviously increases and the ceramic seems to become denser. Our previous study revealed that the densification temperature of pure ZMS is over 1170°C [10]. It can be considered that CBS glass with low melting point (about 670°C [11]) serving as liquid phases promote the grain growth as well as the densification of the ceramics during the sintering process. Moreover, 3 and 4 wt.% CBS-doped ZMS ceramics exhibit two grain shapes: small variform grains and large rod-like grains, as shown in Figure 2b and 2d. The small grains are certainly the $(Zn_{0.8}Mg_{0.2})_2SiO_4$ phase. In order to verify whether the rod-shaped grains are secondary phases, XRD analysis was performed for specimens with 1 and 4 wt.% CBS addition and the results are illustrated in Figure 3. In the case of 1 wt.% CBS-doped sample, only diffraction peaks index to $ZnSiO_4$ as the main crystalline phase are observed. And not any other secondary phases are detected in the case of 4 wt.% CBS-doped one. This result indicates that the elongated grains are not the second-phase and 1 ~ 4 wt.% CBS addition can not influence the crystal phases and form the secondary phases.

Figure 4 shows the dielectric constant (ε_r) of ZMS ceramics with different CBS additions versus the sintering temperature. It can be seen that for almost all the samples, ε_r values increase steady with increasing the sintering temperature and then saturate. It is worth to notice that the sintering temperature of the maximal ε_r value decrease from 980 to 950°C when CBS content increasing from 1 ~ 2 wt.% to 3 ~ 4 wt.%.

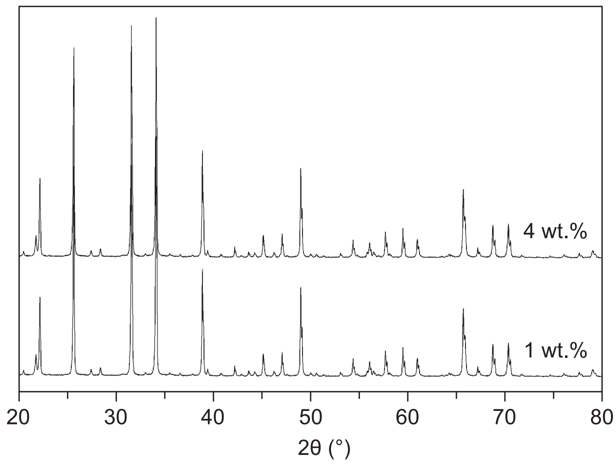
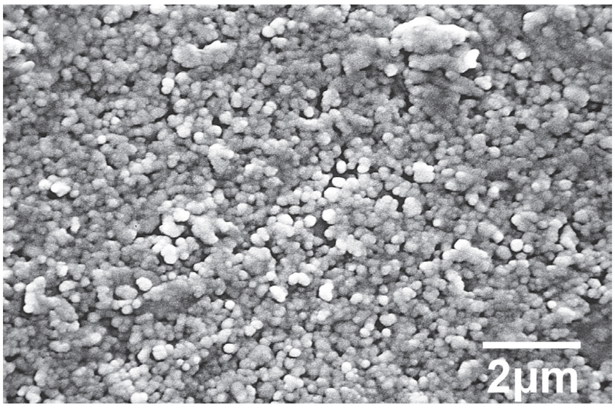
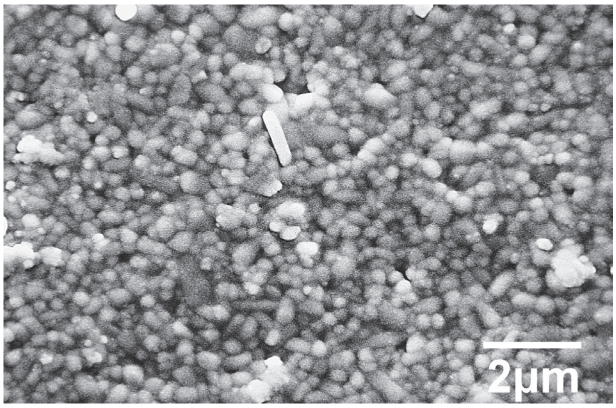


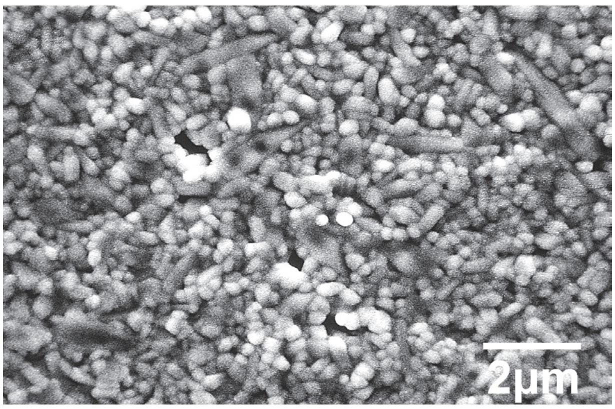
Figure 3. XRD patterns of $(Zn_{0.8}Mg_{0.2})_2SiO_4$ with different amount of CBS glass sintered at 950°C.



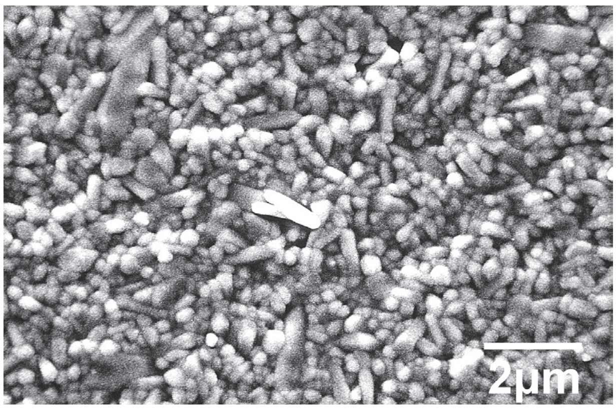
a) 1 wt.%



b) 2 wt.%



c) 3 wt.%



d) 4 wt.%

Figure 2. SEM micrographs of ZMS ceramics with various amount of CBS glass sintered at 950°C.

Moreover, ε_r values in general are enhanced gradually by increasing the doping content of CBS at the same firing temperature. These phenomena suggest that CBS can remarkably lower the sintering temperature of ZMS ceramics, and ZMS ceramics with CBS addition can be densified at lower temperatures of 950~980°C. It is concluded that the decrease of sintering temperature as well densification temperature is caused by liquid-phase effect of CBS additives.

At the same time, the *Q·f* values of ZMS ceramics with CBS glass as a function of the sintering temperature are depicted in Figure 5. For specimens with 1 and 2 wt.% CBS, the *Q·f* values increase gradually with the increase of sintering temperature, and reach a maximum value at 980°C then decrease slightly. However, when the amount of CBS is more than 3 wt.%, the maximal *Q·f* values are obtained at 950°C, and further increase of sintering temperature lead to the significant decrease of *Q·f* values. This is probably due to the formation of porous structure via the volatilization of borium. For 4 wt.% CBS-doped sample, the degradation of *Q·f* values is owing to the formation of liquid phases and the abnormal growth of grains. Thus, it is important to recognize that the CBS glass also play a role in the contribution to the microwave properties of the ZMS sintered ceramics.

Figure 6 shows the XRD patterns of ZMS-CBS ceramic modified by TiO_2 additions sintered at 950°C. It is found that the specimens with ≤ 12 wt.% TiO_2 show Zn_2SiO_4 as the main crystal phase and TiO_2 as the secondary phase. And when the added TiO_2 increases, the intensity of diffraction peaks of TiO_2 is enhanced gradually. This result indicates that only composite mixing effect occurs between Zn_2SiO_4 and TiO_2. That is, the solid solubility of TiO_2 in Zn_2SiO_4 is relative small and these two constitutes can not react each other to form other phases. This is consistent with the results of Zn_2SiO_4–TiO_2 system reported by Guo et al. [1].

The SEM micrographs of ZMS-CBS ceramic with various amount of TiO_2 sintered at 950°C are illustrated in Figure 7. Compared with the TiO_2 undoped sample, it can be observed that the ceramics with 6 and 8 wt.% TiO_2 contain three kinds of grains: small round grains (~1μm) and stick grains (~2 μm) as well as a few of large platy grains (~5 μm), as shown in Figures 7a and 7b. The presence of large grains is probably due to the formation of eutectic liquid phases, which resulted from the reaction between CBS and TiO_2. With the increase of TiO_2 concentration, the large anomalistic grains disappear and the grains become small and uniform significantly. And two kinds of grains with different sizes could be found from the SEM figures (Figures 7c and 7d). The stick grains and round white grains seem to be the ZMS and TiO_2 phases, respectively. Thus, the abnormal grain growth phenomenon is restrained by the pinning effect of TiO_2 second phase at the grain boundary as well as the higher sintering temperature of TiO_2 dielectrics (~1450°C).

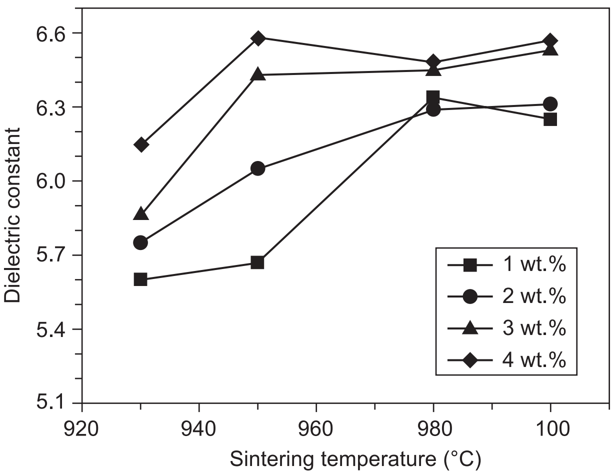


Figure 4. Dielectric constant of $(Zn_{0.8}Mg_{0.2})_2SiO_4$ ceramics with various CBS additions versus the sintering temperature.

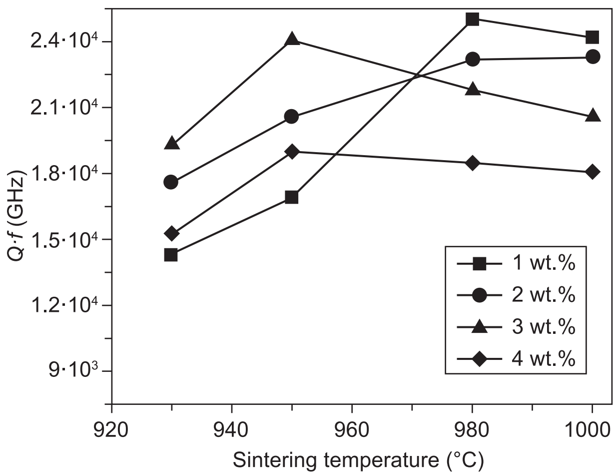


Figure 5. *Q·f* values of $(Zn_{0.8}Mg_{0.2})_2SiO_4$ ceramics with various CBS glass as a function of the sintering temperature.

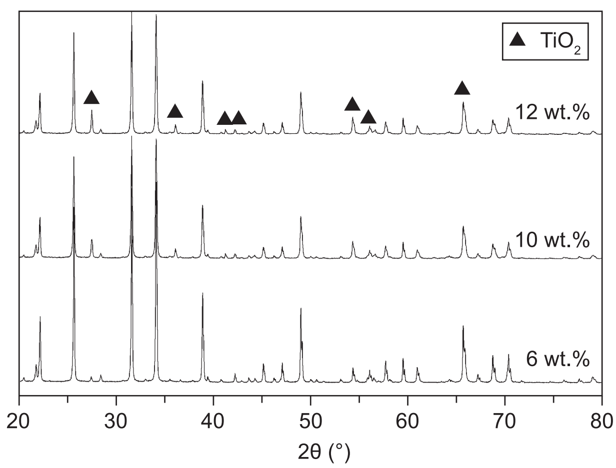
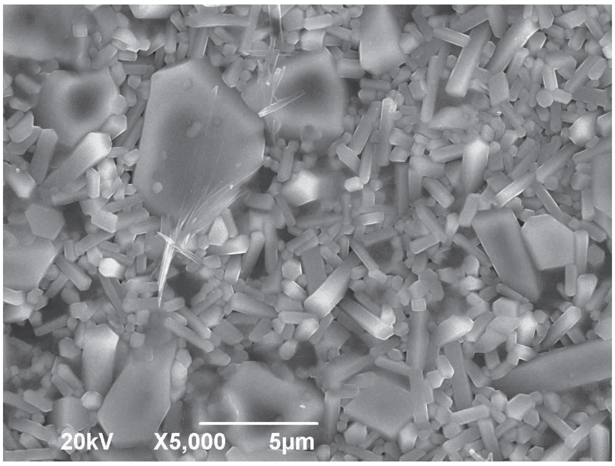
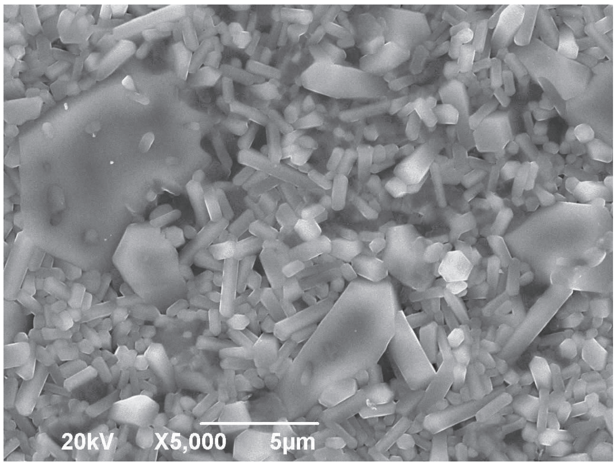


Figure 6. XRD patterns of ZMS-CBS ceramics with different TiO_2 contents sintered at 950°C.

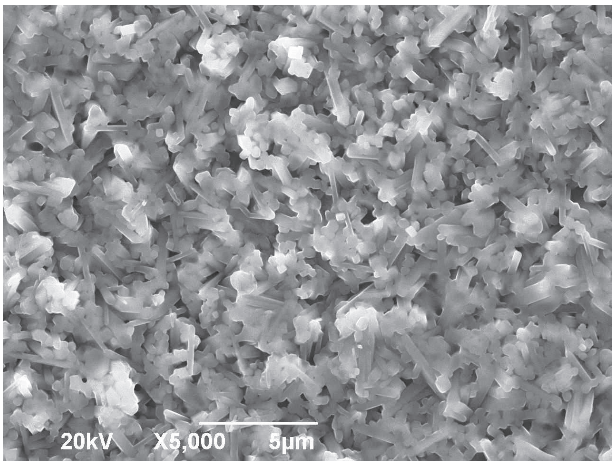
Figure 8 shows the microwave properties of different amount of TiO_2 modified ZMS-CBS ceramics sintered at 950°C. The ε_r, $Q \cdot f$ and τ_f values of this system increases gradually with increasing the doping content of TiO_2, because of the high performance of TiO_2 (ε_r = 100, $Q \cdot f$ = 48000 GHz and τ_f = 450 ppm/°C [12]). For specimens with 6 and 8 wt.% TiO_2, the $Q \cdot f$ exhibit rather low values (14 000 GHz). This may be ascribed to



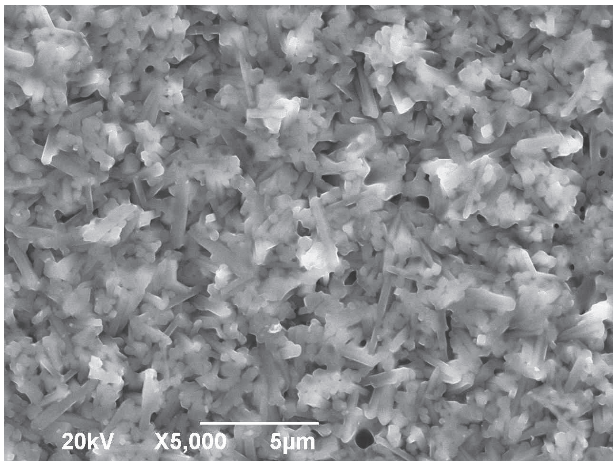
a) 6 wt.%



b) 8 wt.%



c) 10 wt.%



d) 12 wt.%

Figure 7. SEM micrographs of ZMS-CBS ceramic with various amount of TiO_2 sintered at 950°C.

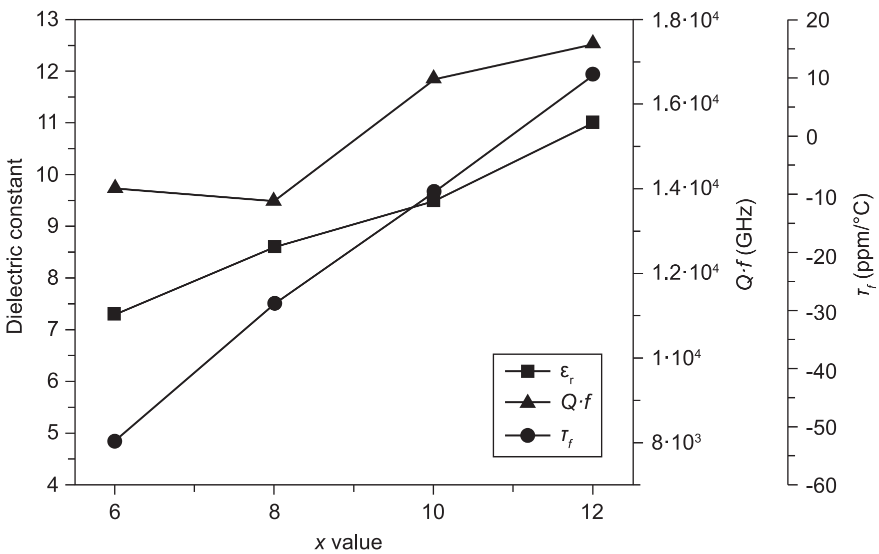


Figure 8. Microwave properties of ZMS-CBS ceramics sintered at 950°C as a function of TiO_2 content.

the formation of eutectic liquid phases and the abnormal growth of grains. In addition, the τ_f value increased from negative (-52.5 ppm/°C) to positive (+12 ppm/°C), and it may be deduced that a zero τ_f value could be attained at about 11 wt.% TiO_2 addition. The ZMS–0.1TiO_2 dielectrics with 3 wt.% CBS sintered at 950°C exhibited the optimal microwave properties: $\varepsilon_r = 9.5$, $Q{\cdot}f = 16\,600$ GHz and $\tau_f = -9.6$ ppm/°C.

CONCLUSION

Microwave properties of $(Zn_{1-x}Mg_x)_2SiO_4$ prepared by the sol-gel process are strongly correlated with the fraction of Mg substitution, and $(Zn_{0.8}Mg_{0.2})_2SiO_4$ sintered at 1170°C could obtain the best characteristics: $\varepsilon_r = 6.3$, $Q{\cdot}f = 189\,800$ GHz and $\tau_f = -63$ ppm/°C. More-over, $CaO–B_2O_3–SiO_2$ (CBS) glass with low melting point could produce the liquid phases during the sintering process and effectively reduce the firing temperature of ZMS dielectrics from 1170 to 950°C, and significantly improve the sintering behavior and microwave properties of ZMS ceramics. 3 wt.% CBS doped $(Zn_{0.8}Mg_{0.2})_2SiO_4$ ceramics sintered at 950°C showed the good microwave characteristics of $\varepsilon_r = 6.4$ and $Q{\cdot}f = 24\,100$ GHz. In addition, because of the limited solubility of TiO_2 in ZMS matrix, TiO_2 act as a secondary phase and form the biphasic structure. The abnormal grain growth is restrained by the pinning effect of TiO_2 second phase at the grain boundary. With increasing the addition of TiO_2, the ε_r, $Q{\cdot}f$ and τ_f values of specimens increase gradually. $(Zn_{0.8}Mg_{0.2})_2SiO_4$ codoped with 3 wt.% CBS and 10 wt.% TiO_2 sintered at 950°C for 2 h exhibited the dense microstructure and excellent microwave properties: $\varepsilon_r = 9.5$, $Q{\cdot}f = 16\,600$ GHz and $\tau_f = -9.6$ ppm/°C.

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