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Effect of ZnO additive on sintering behavior and microwave dielectric properties of $0.95MgTiO_3$–$0.05CaTiO_3$ ceramics

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Abstract

The effects of ZnO additive on the microstructures, the phase formation and the microwave dielectric properties of $MgTiO_3$–$CaTiO_3$ ceramics were investigated. The sintering temperature of ZnO-doped $0.95MgTiO_3$–$0.05CaTiO_3$ ceramics can be lowered to 1300 °C due to the liquid phase effect. Formation of second phase $MgTi_2O_5$ can be effectively restrained through the addition of ZnO. The microwave dielectric properties are found strongly correlated with the sintering temperature as well as the amount of ZnO addition. At 1300 °C, $0.95MgTiO_3$–$0.05CaTiO_3$ ceramics with 1 wt% ZnO addition possesses a dielectric constant ε_r of 20, a $Q \times f$ value of 65,000 (at 7 GHz) and a τ_f value of −5.8 ppm/°C. In comparison with pure $0.95MgTiO_3$–$0.05CaTiO_3$ ceramics, the doped sample shows not only a 16% loss reduction but also a lower sintering temperature. That makes it a very promising material to replace the present one for GPS patch antennas.

Keywords: $MgTiO_3$–$CaTiO_3$; Low loss; Dielectric properties; Liquid phase sintering

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1. Introduction

Development of microwave dielectric resonators and antennas for applications in communication systems such as cellular phone, direct broadcasting satellite (DBS) and global positioning systems has been rapidly progressing in the past decade [1,2]. An advantage of using dielectric resonators is making the size reduction of microwave components possible. Requirements for these dielectric resonators must be the combined dielectric properties of a high dielectric constant ($\varepsilon_r > 20$), a low dielectric loss ($Q > 5000$, where $Q = 1/\tan\delta$) and a near-zero temperature coefficient of resonant frequency (τ_f). These three parameters are correlated to the size, frequency selectivity and temperature stability of the system, respectively. To satisfy the demands of microwave circuit designs, each dielectric property should be precisely controlled.

$MgTiO_3$–$CaTiO_3$ (hereafter referred to as MCT) ceramics is well known as the material for temperature compensating type capacitor and dielectric resonator. Especially, it has been widely applied in today's GPS patch antenna manufacturing. The material is made of a mixture of magnesium titanate ($MgTiO_3$: $\varepsilon_r \sim 17$, $Q \times f$ value ~160,000 at 7 GHz and τ_f value ~−45 ppm/°C) [3] and calcium titanate ($CaTiO_3$: $\varepsilon_r \sim 170$, $Q \times f$ value ~3600 at 7 GHz and τ_f value ~800 ppm/°C) [4]. With the ratio Mg:Ca = 95:5, $0.95MgTiO_3$–$0.05CaTiO_3$ (hereafter referred to as 95MCT) ceramics gives $\varepsilon_r \sim 20$, $Q \times f$ ~56,000 at 7 GHz, and a zero τ_f value. However, it required sintering temperatures as high as 1400–1450 °C. Many researchers made efforts to study the microstructures and the microwave dielectric properties of the 95MCT ceramics by adding various additives or varying the processing. Ferreriar et al. had serious reports on the microwave dielectric properties of the 95MCT. The dielectric properties of 95MCT ceramics can be further improved by introducing additions such as Cr, La, B and Bi [5–9]. The MCT ceramics prepared by chemical technique could be sintered at lower temperature and gave excellent dielectric

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properties ($\varepsilon_r \sim 19.1$, $Q \times f$ value ~84,800 at 8 GHz, τ_f value: unreported). However, the chemical process often required an expensive and time-consuming flexible process. The liquid-phase sintering by adding glass or low melting point materials was found to effectively lower the firing temperature [10]. In this paper, ZnO was added to $0.95MgTiO_3$–$0.05CaTiO_3$ ceramic system as a sintering aid to lower its sintering temperature. The resultant microwave dielectric properties were analyzed based upon the densification, the X-ray diffraction patterns and the microstructures of the ceramics. The correlation between the microstructure and the $Q \times f$ value was also investigated.

2. Experimental procedures

Samples of $MgTiO_3$ and $CaTiO_3$ were individually synthesized by conventional solid-state methods from high-purity oxide powders (>99.9%): MgO, $CaCO_3$ and TiO_2. The starting materials were mixed according to the stoichiometry: $MgTiO_3$ and $CaTiO_3$ and ground in distilled water for 8 h in a balling mill with agate balls (ZrO_2). Both mixtures were dried and calcined at 1100 °C for 4 h. The calcined powders were mixed as desired composition $(1-x)MgTiO_3$–$xCaTiO_3$ with different amounts of ZnO additions as sintering aids and re-milled for 8 h and then sieved using a 100 mesh screen. The sieved powders were add with an organic binder (PVA) and pressed into disks with dimensions of 11 mm in diameter and 5 mm in thickness. The pellets were sintered at temperatures of 1150–1350 °C for 4 h in air. The heating and cooling rates of the samples were 10 °C/min.

The densities of the sintered ceramics were measured using the Archimedes method. The crystalline phases were analyzed by means of the X-ray powder diffraction method using Cu Kα radiation from 20° to 60° in 2θ. The scanning rate was 4°/min. The microstructure was observed using a scanning electron microscope (SEM). The dielectric constants and the unloaded Q values were measured by employing the Hakki and Coleman method [11]. The apparatus consisted of parallel conducting brass plates and coaxial probes connected to a HP8757D network analyzer and a HP8350B sweep oscillator. Identical technique was applied in measuring the temperature coefficient of resonant frequency (τ_f). The test set was placed over a thermostat in the temperature range from 25 to 80 °C. The τ_f value (ppm/°C) can be calculated by noting the change in resonant frequency (Δf):

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \tag{1}$$

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

3. Results and discussion

3.1. Phases and microstructures

The XRD patterns of 1 wt% ZnO-doped 95MCT ceramics at different sintering temperatures are shown in Fig. 1. Ilmenite structures were observed for all compositions. It is understood that the $MgTiO_3$–$CaTiO_3$ ceramics is an eutectic composite containing crystals of two compounds, $MgTiO_3$: trigonal (ICDD #06-0494) and $CaTiO_3$: orthorhombic (ICDD #22-0153). Second phase $MgTi_2O_5$, usually formed as an intermediate phase during the growth, was identified and difficult to completely eliminate from the sample prepared by mixed oxide route. Formation of second phase was attributed to the LOI of MgO resulting in a Ti-rich phase $MgTi_2O_5$. In this study, however, second phase $MgTi_2O_5$ was almost not detectable. Since the ionic radius of Zn^{2+} (0.083 nm) is similar to that of Mg^{2+} (0.078 nm), the position of Mg^{2+} can be occupied by the ion of Zn^{2+} to form $(Mg,Zn)TiO_3$ composition and will not cause charge distortion. Solid solution has been shown for low level Zn replacement such as $(Mg_{0.95}Zn_{0.05})TiO_3$. Exceeding Mg will compensate Ti-rich phase to form $MgTiO_3$. It rationalizes the elimination of second phase $MgTi_2O_5$ can be achieved by adding ZnO to the $MgTiO_3$–$CaTiO_3$ ceramic system. Similar X-ray diffraction patterns (not shown) were identified for samples with different ZnO additions and second phase $MgTi_2O_5$ was almost eliminated. These results suggested that ZnO addition not only contributes in lowering the sintering temperature but also inhibits the formation of second phase of 95MCT ceramics.

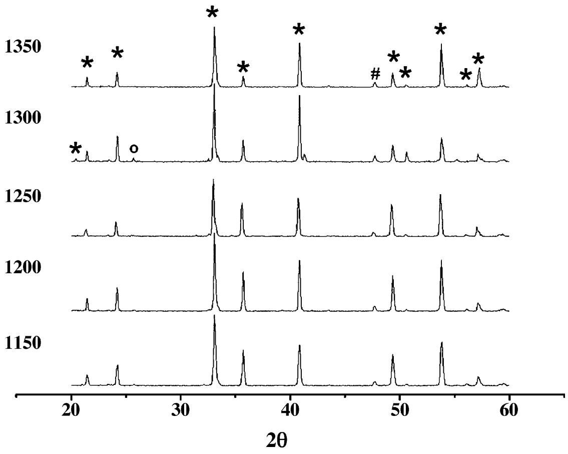

Fig. 1. X-ray diffraction patterns of $0.95MgTiO_3$–$0.05CaTiO_3$ ceramics with 1 wt% ZnO additions at different sintered temperature (⋆: $MgTiO_3$, □: $CaTiO_3$, ○: $MgTi_2O_5$).

The SEM photographs of 95MCT ceramics with 1 wt% ZnO addition at different sintering temperatures for 4 h are illustrated in Fig. 2. The 95MCT ceramics was not dense and the grain did not grow at 1150 °C. The grain size of 95MCT increased continuously with the increase of sintering temperature. For liquid sintering of ceramics, the liquid phase would be resident or disappear in the final stage. With 1 wt/% ZnO addition, the pores were almost eliminated for specimen sintered at 1300 °C due to the effect of liquid phase and the grain growth rapidly increased above 1300 °C. It also revealed non-uniform grain morphology.

The plots of apparent density of 95MCT ceramics with various amounts of ZnO additions versus the sintering temperature are shown in Fig. 3. The density of the 95MCT ceramics increased with increasing sintering temperature and saturated at 1250 °C. The increase in the density was due to the elimination of pore as observed in Fig. 2. However, it slightly decreased at temperatures higher than 1250 °C for specimens with 5 wt% ZnO additions owing to a rapid grain growth. The decrease in the density also could be caused by the evaporation of Zn at high temperature. Moreover, higher ZnO content resulted in higher density implying that ZnO could effectively promote the densification of the ceramics. For 95MCT with 1 wt% ZnO addition, the maximum apparent density was obtained at 1300 °C.

3.2. Microwave dielectric properties

Fig. 4 shows the dielectric constants of 95MCT ceramics with different amounts of ZnO additions as functions of their sintering

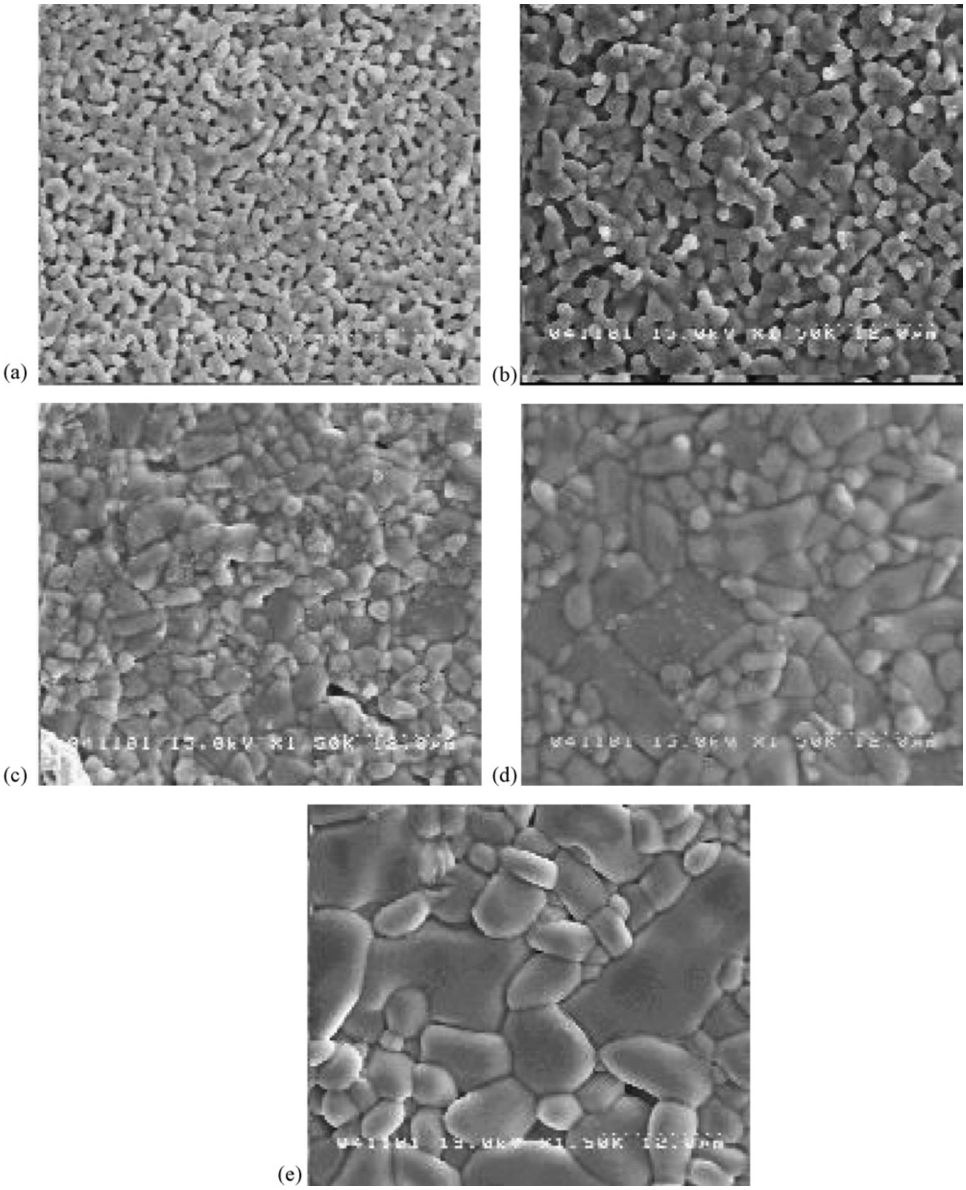

Fig. 2. SEM photographs of $0.95MgTiO_3$–$0.05CaTiO_3$ ceramics with 1 wt% ZnO addition sintered at (a) 1150 °C, (b) 1200 °C, (c) 1250 °C, (d) 1300 °C, and (e) 1350 °C for 4 h.

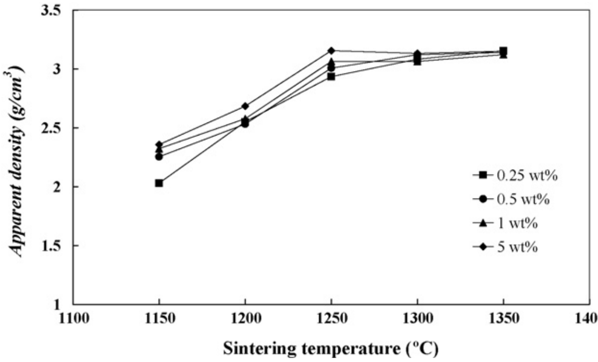

Fig. 3. Apparent density of ZnO-doped $0.95MgTiO_3$–$0.05CaTiO_3$ ceramics as a function of sintering temperature.

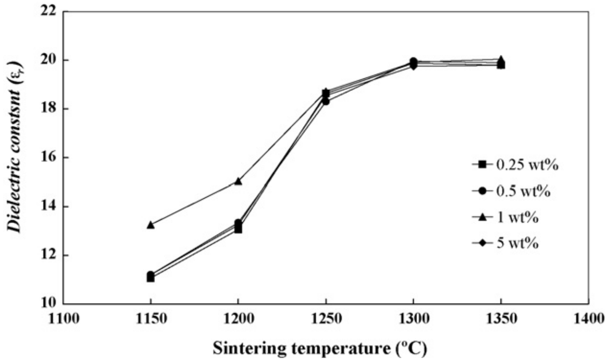

Fig. 4. The ε_r value of ZnO-doped $0.95MgTiO_3$–$0.05CaTiO_3$ ceramics as a function of sintering temperature.

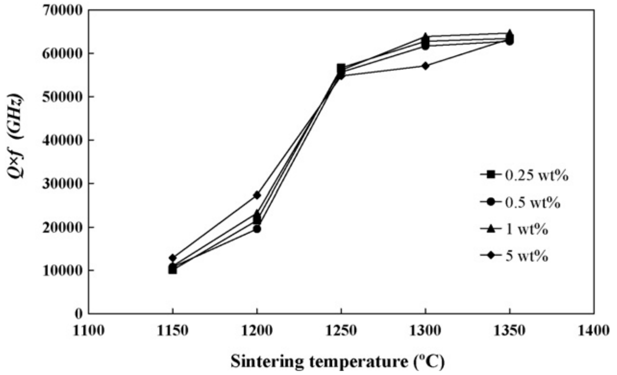

Fig. 5. The $Q \times f$ values of ZnO-doped $0.95MgTiO_3$–$0.05CaTiO_3$ ceramics as a function of sintering temperature.

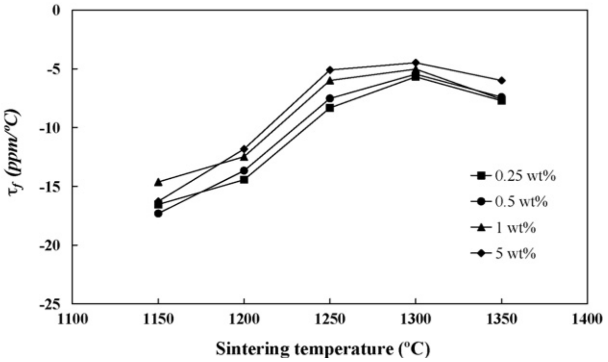

Fig. 6. The τ_f value of ZnO-doped $0.95MgTiO_3$–$0.05CaTiO_3$ ceramics as a function of sintering temperature.

temperatures. The dielectric constant increased with increasing sintering temperature and started to saturate at 1250 °C. The relationships between ε_r values and sintering temperatures revealed the same trend with those between densities and sintering temperatures since higher density represents lower porosity. The ε_r value of the 95MCT ceramics with 1 wt% ZnO addition increased from 13.36 to 20.31 as the sintering temperature increased from 1150 to 1350 °C.

The quality factor values ($Q \times f$) of 95MCT ceramics with various ZnO additions at different sintering temperatures are demonstrated in Fig. 5. Density plays an important role in controlling the dielectric loss, and has been shown for other microwave dielectric materials. With increasing sintering temperature, the $Q \times f$ value was found to increase, which was consistent with the variation of density. Kucheiko et al. reported that the $Q \times f$ values increased with the average grain size [12]. As the grain size increased, the pores and the grain boundary area decreased, thus reducing the lattice imperfections and increasing the $Q \times f$ values [12,13]. The increases in $Q \times f$ values were attributed to the increases in densities and grain growth. As observed in Fig. 2, inhomogeneous grain growth appeared at higher sintering temperature (1350 °C), which revealed an increase in lattice imperfection and dielectric loss was then increased. The saturation in $Q \times f$ values could be a result from the non-uniform grain morphology. The microwave dielectric loss is mainly caused not only by the lattice vibration modes, but also by the pores, the second phases, the impurities, or the lattice defect [14]. As discussed in Fig. 1, the addition of ZnO seemed to inhibit the formation of $MgTi_2O_5$ which might also increase the $Q \times f$ value of 95MCT ceramics [3]. At 1300 °C, a maximum $Q \times f$ value of 65,000 (at 7 GHz) was obtained at the level of 1 wt% ZnO addition for the 95MCT ceramics, which was 16% higher than that of the un-doped one. Moreover, it also revealed a 150 °C temperature reduction (1450 → 1300 °C) in comparison with the pure 95MCT ceramics.

Fig. 6 presents the temperature coefficient of resonant frequency (τ_f) for the 95MCT ceramics with various amounts of ZnO additions as a function of sintering temperature. The τ_f value is basically related to the composition and the second phase of the material. As observed in Fig. 6, the τ_f value varied toward positive with increasing ZnO content. It might be attributed to the existence of $ZnTiO_3$ possessing a positive τ_f (~40 ppm/°C). A breaking point appears at 1300 °C and the variation of τ_f becomes downward due to the decrease of $ZnTiO_3$ phase resulted from Zn evaporation as the sintering temperature rises above 1300 °C [15]. The Zn position was most likely occupied by exceeding Mg to form $MgTiO_3$. With 1 wt% ZnO addition, a τ_f value of −5.8 ppm/°C can be achieved for specimen at 1300 °C.

4. Conclusion

The dielectric properties of $MgTiO_3$–$CaTiO_3$ ceramics with ZnO addition were investigated. $0.95MgTiO_3$–$0.05CaTiO_3$ ceramics exhibited mixed phases of $MgTiO_3$ as the main phase in associate with some minor phases $CaTiO_3$ and $MgTi_2O_5$. The ZnO additive can not only effectively lower the sintering temperature but also promote $Q \times f$ values. Moreover, it also inhibits the formation of second phase $MgTi_2O_5$. Comparing to pure 95MCT ceramics sintered at 1450 °C, the $Q \times f$ value of 1 wt% ZnO-doped 95MCT increased from 56,000 to 65,000 GHz as the sintering temperature lowered from 1450 to 1300 °C. It also possesses compatible dielectric constant ε_r of 20 and τ_f value of −5.8 ppm/°C.

Acknowledgment

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