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Microstructures and microwave dielectric properties of low-temperature sintered $Ca_2Zn_4Ti_{15}O_{36}$ ceramics

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Abstract Low-temperature sintered $Ca_2Zn_4Ti_{15}O_{36}$ microwave dielectric ceramic was prepared by conventional solid state reaction method. The influences from V_2O_5 addition on the sintering behavior, crystalline phases, microstructures and microwave dielectric properties were investigated. The crystalline phases and microstructures of $Ca_2Zn_4Ti_{15}O_{36}$ ceramic with V_2O_5 addition were investigated by X-ray diffraction, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). V_2O_5 addition lowered the sintering temperature of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics from 1140 °C to 930 °C. $Ca_2Zn_4Ti_{15}O_{36}$ ceramic with 5wt% V_2O_5 addition could be densified well at 930 °C, and showed good microwave dielectric properties of $\varepsilon_r \sim 46$, $Q \times f \sim 13400$ GHz, and temperature coefficient of resonant frequency (τ_f) ~ 164 ppm/°C.

1 Introduction

Recently, the development of low temperature co-fired ceramics (LTCC) has caused much interest because the multilayer devices have been widely applied for the miniaturization of microwave dielectric components [1]. Multilayer devices require the dielectric ceramics being cofirable with the internal metallic electrode. Ag and Cu have been widely used as metallic electrodes because of their high conductivities and low cost, and their melting temperatures are 961 and 1064 °C, respectively [2, 3]. Therefore, it is necessary for microwave dielectric ceramics that could be sintered at a low temperature and thus be cofirable with Ag or Cu. Several low melting oxides or their composites have been used to reduce the sintering temperature, such as V_2O_5, Bi_2O_3, Li_2O, LiF, CuO, B_2O_3 or some types of synthetic glasses [4–7], which could decrease the sintering temperature efficiently by liquid sintering, forming solid solutions or reacting with base materials.

$Ca_2Zn_4Ti_{15}O_{36}$ composition was first reported by Kim et al. [8] on their investigation on calcium modified zinc titanate, which was also the first report of the microwave dielectric properties ($\varepsilon_r \sim 47$, $Q \sim 4120$, $\tau_f \sim +120$ ppm/°C) of this compounds. However, they pointed out that a single-phase of $Ca_2Zn_4Ti_{15}O_{36}$ cannot be obtained via solid state reaction method. Yue et al. [9] fabricated the single-phase of $Ca_2Zn_4Ti_{15}O_{36}$ through a citrate sol-gel process and they reported its microwave dielectric properties ($\varepsilon_r \sim 48.1$, $Q \times f \sim 27000$ GHz, $\tau_f \sim +53.5$ ppm/°C) sintered at 1100 °C. They also fabricated a similar compounds $Ca_2Zn_4Ti_{16}O_{38}$ in the same method and reported its microwave dielectric properties ($\varepsilon_r \sim 47$–49, $Q \times f \sim 27800$–31600 GHz, $\tau_f \sim +45$–50 ppm/°C) [10]. $Ca_2Zn_4Ti_{15}O_{36}$ ceramic would be a good candidate for LTCC application if its sintering temperature could be lowered to below 960 °C.

In this work, V_2O_5 was used as sintering aids to lower the sintering temperature of $Ca_2Zn_4Ti_{15}O_{36}$ ceramic. The sintering behavior, crystalline phases, microstructures and microwave dielectric properties were reported and their relations were also discussed.

2 Experimental procedures

The $Ca_2Zn_4Ti_{15}O_{36}$ compositions with 0–5wt% V_2O_5 addition were prepared by conventional solid state reaction

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method using high purity $CaCO_3$ (>99%, Guo-Yao Co. Ltd., Shanghai, China), ZnO (>99%, Guo-Yao Co. Ltd., Shanghai, China), rutile TiO_2 (>99%, Guang Dong Zhaoqing, China) and V_2O_5 (>99%, Guo-Yao Co. Ltd., Shanghai, China). The raw materials were weighed according to the compositions of $Ca_2Zn_4Ti_{15}O_{36}$ and milled with ZrO_2 balls (2 mm in diameter) for 4 h in ethanol. The mixtures were then dried and calcined at 950 °C for 4 h. The calcined powders were mixed with different amounts of V_2O_5 additives as sintering aids and re-milled for 5 h with ZrO_2 balls in ethanol. After drying, the powders were uniaxially pressed into disks of 10 mm in diameter and 5 mm in thickness. The cylinders were then sintered in air at 875–1200 °C for 2 h.

The crystalline phases of the samples were investigated using X-ray diffractometry with CuKα radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). These specimens were ground with SiC sandpaper and polished using 1/4 μm diamond paste. The microstructures of the sintered samples were observed on the polished surfaces, after thermal etching at 900 °C for 30 min, with scanning electron microscopy (SEM) (JEOL JSM-6460, Japan) coupled with energy-dispersive X-ray spectroscopy (EDS). The densities of the sintered specimens, as a function of sintering temperature, were measured by Archimedes method. Dielectric behaviors at microwave frequency were measured at a frequency of 4–6 GHz by the $TE_{01\delta}$ shielded cavity method with a network analyzer (8720ES, Agilent, Palo Alto, USA) and a DELTA 9023 temperature chamber (Delta Design, Poway, USA). Temperature coefficient of resonant frequency τ_f was calculated from the following equation:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25} \times 60} \times 10^6 (\mathrm{ppm}/^{o}\mathrm{C}) \quad (1)$$

where f_{85} and f_{25} are the resonant frequencies of dielectric resonator at 85 °C and 25 °C, respectively.

3 Results and discussion

3.1 Crystalline phases and microstructures

Figure 1 shows the XRD patterns of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics with 0–5 wt% V_2O_5 addition. It was found that most of the diffraction peaks of sintered $Ca_2Zn_4Ti_{15}O_{36}$ ceramics with 0–0.5 wt% V_2O_5 addition could be indexed as rhombohedral $Ca_2Zn_4Ti_{15}O_{36}$ phase (PDF Number: 34-0055), a small amount of Zn_2TiO_4 phase (PDF Number: 25-1164) and residual tetragonal rutile phase (PDF Number: 21-1276), $CaTiO_3$ phase (PDF-39-0145) were also detected. SEM micrographs of the sintered pure $Ca_2Zn_4Ti_{15}O_{36}$ ceramic (as shown in Fig. 3a, b) presents that most of the

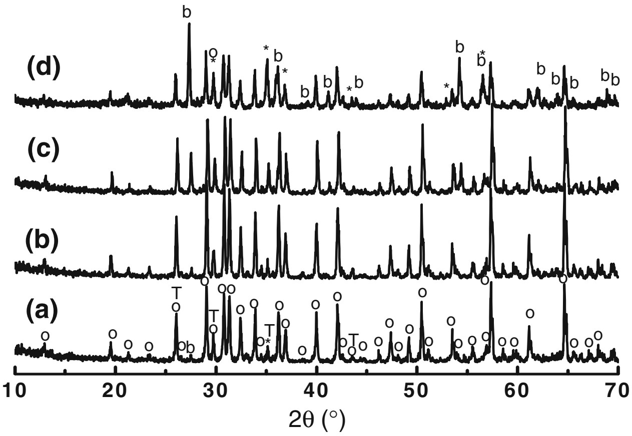

Fig. 1 XRD patterns of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics with x wt% V_2O_5 addition: (a) x = 0 sintered at 1170 °C; (b) x = 0.5 sintered at 1140 °C; (c) x = 3 sintered at 1110 °C and (d) x = 5 sintered at 960 °C; (o: $Ca_2Zn_4Ti_{15}O_{36}$ phase, b: rutile TiO_2 phase, *: Zn_2TiO_4 phase, PDF-25-1164, T: $CaTiO_3$ phase, PDF-39-0145)

grains showed anomalous shape like cobblestones. Meanwhile, a small amount of smaller grains with sharp angles were also observed existing in the grain binderies. EDS analysis (Fig. 3g) showed that the chemical composition of the anomalous cobblestone-like grains and the small grains were similar to $Ca_2Zn_4Ti_{15}O_{36}$ and $CaTiO_3$, respectively. According to the results that reported by Kim et al. [8] and Yue et al. [9], the following reactions might occur during the formation process of $Ca_2Zn_4Ti_{15}O_{36}$ phase:

$$TiO_2 + CaCO_3 \xrightarrow{600\text{–}800^\circ C} CaTiO_3 + CO_2 \quad (2)$$

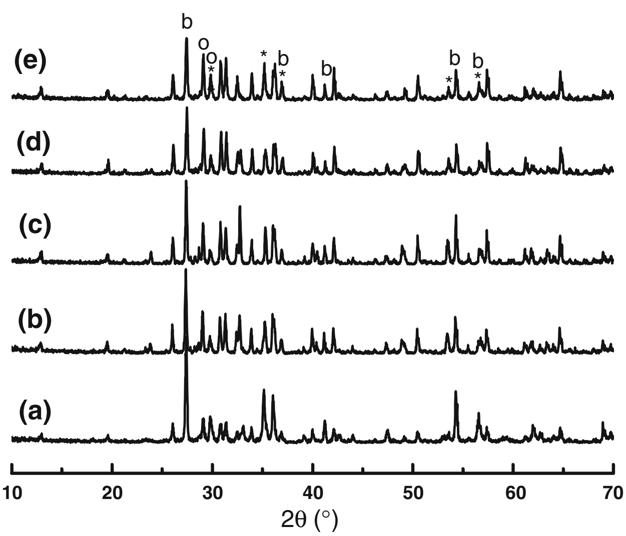

Fig. 2 XRD patterns for powders of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics with 5 wt% V_2O_5 addition sintered at (a) 600 °C; (b) 800 °C; (c) 850 °C; (d) 950 °C for 2 h; (o: $Ca_2Zn_4Ti_{15}O_{36}$ phase, b: rutile TiO_2 phase, *: Zn_2TiO_4 phase)

$$TiO_2 + 2ZnO \xrightarrow{800\text{–}900^\circ C} Zn_2TiO_4 \quad (3)$$

$$2Zn_2TiO_4 + 2CaTiO_3 + 9TiO_2 \xrightarrow{900\text{–}1000^\circ C} Ca_2Zn_4Ti_{15}O_{36} \quad (4)$$

The results from the XRD patterns and SEM micrographs of pure $Ca_2Zn_4Ti_{15}O_{36}$ ceramics in the present work agreed with the results that reported by Kim et al. [8] and Yue et al. [9] When the content of V_2O_5 addition increased to 3Ð5wt%, the tetragonal rutile phase and Zn_2TiO_4 phase increased greatly (as shown in Fig. 1). It means that a reaction between V_2O_5 and $Ca_2Zn_4Ti_{15}O_{36}$ might occur during the sintering process. The reaction between V_2O_5 and $Ca_2Zn_4Ti_{15}O_{36}$ was studied via the XRD patterns of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics with 5wt% V_2O_5 addition sintered at 600Ð950C for 2 h and Fig. 2 presents the XRD patterns. Figure 2 shows that the diffraction peaks of $Ca_2Zn_4Ti_{15}O_{36}$ phase were weak when the $Ca_2Zn_4Ti_{15}O_{36}$ ceramics with 5wt% V_2O_5 addition sintered at 600C, and became stronger when sintered at 800Ð950C.

Figure 3 presents the typical SEM micrographs and EDS analysis of the sintered $Ca_2Zn_4Ti_{15}O_{36}$ ceramics with different amounts of V_2O_5 addition. It was found that a small amount of smaller grains with sharp angles existed in the sintered pure $Ca_2Zn_4Ti_{15}O_{36}$ ceramics matrix, and they did not disappear when the sintering temperature increased to as high as 1170 C. EDS analysis shows that the smaller grains were $CaTiO_3$ grains (as shown in Fig. 3a, g). The results indicate again that a single $Ca_2Zn_4Ti_{15}O_{36}$ phase could be difÞcult to be obtained by conventional solid state reaction method. When 0.5wt% V_2O_5 was added as the sintering aids, the smaller grains with sharp angles disappeared in the sintered ceramic matrix. Perhaps a small amount of V_2O_5 addition was propitious to the formation of $Ca_2Zn_4Ti_{15}O_{36}$ phase. The SEM micrographs of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics

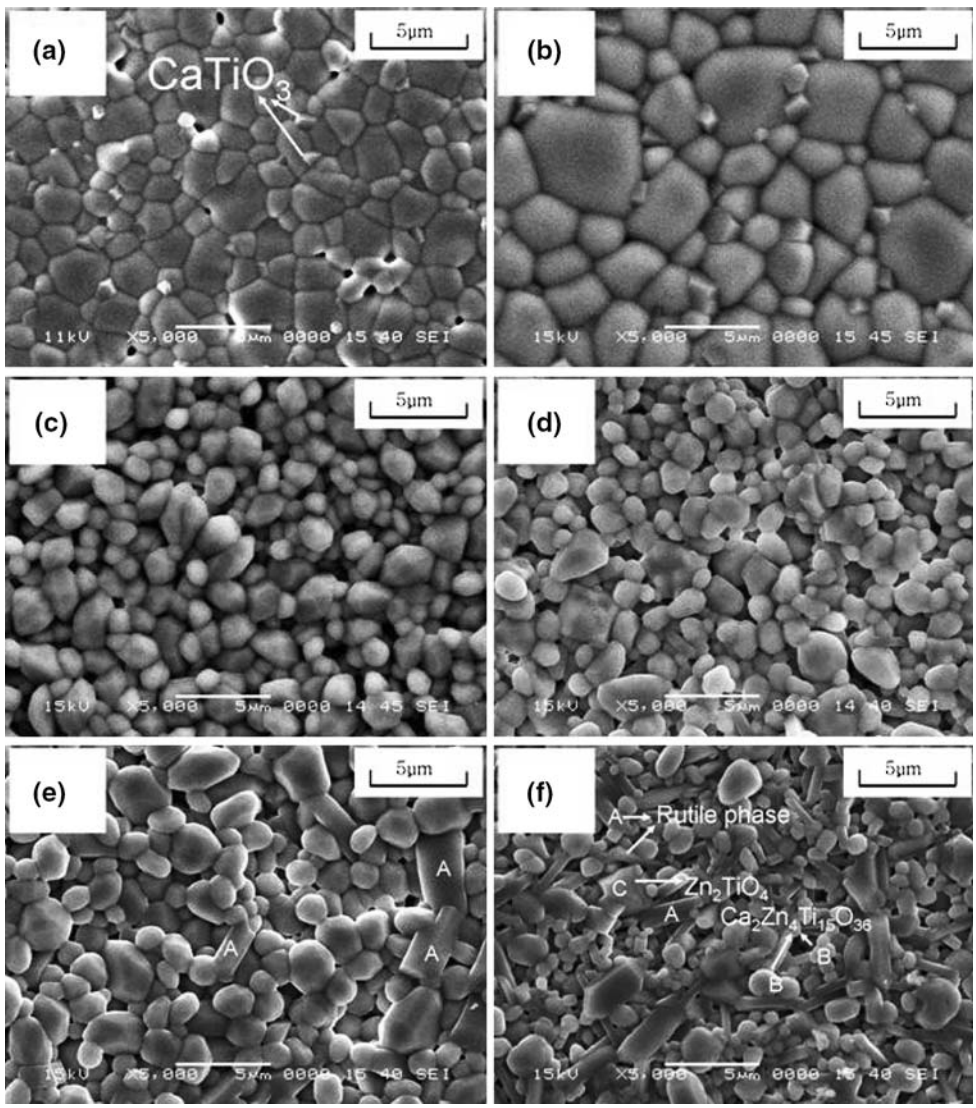

Fig. 3 SEM micrographs for the surface of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics with xwt% V_2O_5 addition: (a) $x = 0$ sintered at 1110 C; (b) $x = 0$ sintered at 1170 C; (c) $x = 0.5$ sintered at 1050 C; (d) $x = 3$ sintered at 930 C; (e) $x = 3$ sintered at 1020 C; (f) $x = 5$ sintered at 930 C; and EDS analysis for $Ca_2Zn_4Ti_{15}O_{36}$ ceramics with xwt% V_2O_5 addition: (g) $x = 0$ sintered at 1110C; (h) $x = 5$ sintered at 930C

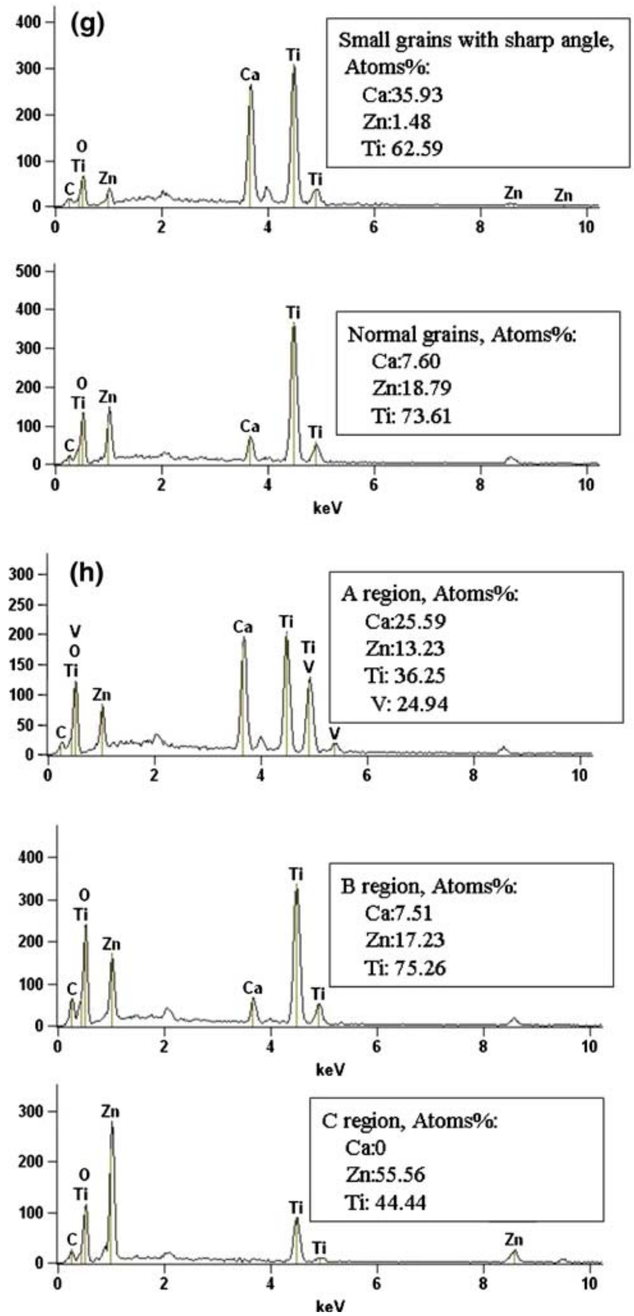

Fig. 3 continued

with 3wt% V_2O_5 addition shows that some abnormal grains (marked as A in Fig. 3e) appeared in the sintered ceramic matrix. When the content of V_2O_5 addition increased to 5wt%, three kinds of separate grains co-existed in the sintered $Ca_2Zn_4Ti_{15}O_{36}$ ceramics (as shown in Fig. 3f). Combining EDS analysis in Fig. 3h with XRD analysis in Fig. 1, it was considered that they were $Ca_2Zn_4Ti_{15}O_{36}$ grains (marked as B in Fig. 3f) and Zn_2TiO_4 grains (marked as C in Fig. 3f), respectively, and the A regions were some kind of $(Ca,Zn)_xV_{2x}Ti_{1-3x}O_2$ grains, whose crystalline phase might be tetragonal rutile phase.

Previous studies [11] showed that Ti^{4+} in rutile TiO_2 could be substituted by a pentavalent cation and a divalent cation and the composition remained rutile solid solutions, such as $Ti_{1-3x}Zn_x(Nb,Ta)_{2x}O_2$. The dielectric properties of these rutile solid solutions were studied in our other works [12]. A rutile solid solution of $(Ca,Zn)_xV_{2x}Ti_{1-3x}O_2$ might be obtained during the sintering process of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics with 3–5wt% V_2O_5 addition in present work. According to the XRD data in Fig. 2, the following reaction might occur during the sintering process of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics with 3–5wt% V_2O_5 addition:

$$Ca_2Zn_4Ti_{15}O_{36} + xV_2O_5 \xrightarrow{<600^\circ C} Zn_2TiO_4 + (Ca,Zn)_x V_{2x}Ti_{1-3x}O_2$$

$$Zn_2TiO_4 + y(Ca,Zn)_xV_{2x}Ti_{1-3x}O_2 \xrightarrow{600\text{–}800^\circ C} x(Ca,Zn)_y V_{2y}Ti_{1-3y}O_2 + Ca_2Zn_4Ti_{15}O_{36}\ (y > x)$$

That is to say the x value of $(Ca,Zn)_xV_{2x}Ti_{1-3x}O_2$ increased with the sintering temperature and reached a constant at about 800°C. The works on $(Ca,Zn)_xV_{2x}Ti_{1-3x}O_2$ will be studied further in the future.

3.2 Densification behaviors

Figure 4 shows the bulk densities of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics with 0–5wt% V_2O_5 addition as a function of sintering temperature. It was found that the bulk density of pure $Ca_2Zn_4Ti_{15}O_{36}$ ceramic increased sharply with the sintering temperature because of the decrease of pores and reached a maximum at 1170°C. The SEM micrographs in

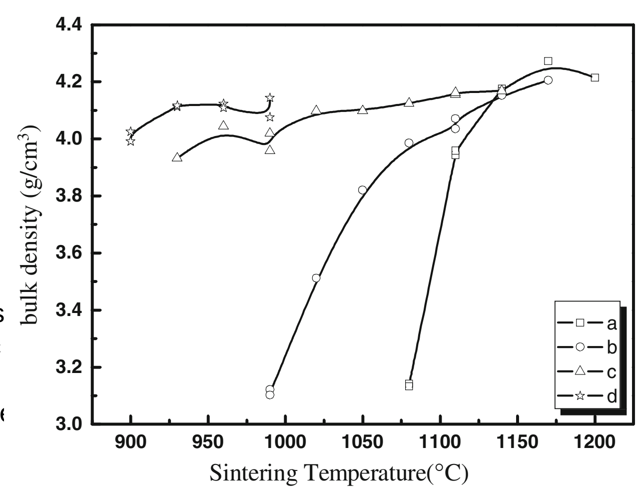

Fig. 4 Bulk densities of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics with xwt% V_2O_5 addition as a function of sintering temperature: (a) $x = 0$; (b) $x = 0.5$; (c) $x = 3$ and (d) $x = 5$

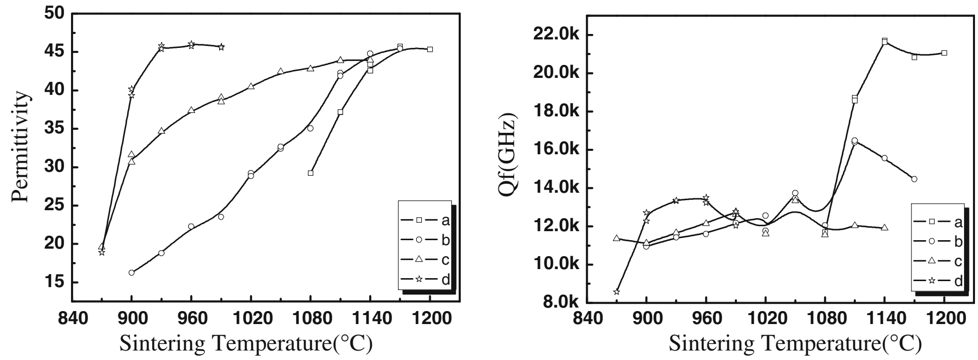

Fig. 5 Microwave dielectric properties of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics with xwt% V_2O_5 addition as a function of sintering temperature: (a) $x = 0$; (b) $x = 0.5$; (c) $x = 3$ and (d) $x = 5$

Fig. 3a shows that a small amount of pores existed in the ceramic matrix that was sintered at 1110°C while a microstructure with the grains well-packed and uniformly distributing with nearly no pores was obtained in the pure $Ca_2Zn_4Ti_{15}O_{36}$ ceramic that was sintered at 1170°C. That is to say that the pure $Ca_2Zn_4Ti_{15}O_{36}$ was difficult to be densified well at about 1110°C. The bulk densities of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics with 3–5wt% V_2O_5 addition increased slightly, and the SEM micrographs in Fig. 3e, f shows that both the $Ca_2Zn_4Ti_{15}O_{36}$ ceramic with 3wt% V_2O_5 addition sintered at 1020°C and that with 5wt% V_2O_5 addition sintered at 930°C presented densified microstructures. It indicates that the $Ca_2Zn_4Ti_{15}O_{36}$ ceramics with 3wt% and 5wt% V_2O_5 addition could be densified well at 1020°C and 930°C, respectively. 5wt% V_2O_5 addition lowered the sintering temperature of $Ca_2Zn_4Ti_{15}O_{36}$ ceramic from 1170°C to 930°C, although V_2O_5 reacted with $Ca_2Zn_4Ti_{15}O_{36}$ during the sintering process. Perhaps the rutile solid solution of $(Ca_xZn_{2y})Ti_{1-3x}O_2$ possesses a low melting temperature, which might be the reason for the low sintering temperature of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics with 3–5wt% V_2O_5 addition.

3.3 Microwave dielectric properties

Figure 5 illustrates the microwave dielectric properties of V_2O_5 doped $Ca_2Zn_4Ti_{15}O_{36}$ ceramics as a function of sintering temperature. In general, dielectric properties depend on grain size, porosity, grain boundary phase, chemical inhomogeneity and domain size [13]. The dielectric constant (ε_r) of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics was mainly influenced by the porosity and crystalline phases. The ε_r value of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics with 0.5wt% V_2O_5 addition sintered at 930°C was 18.8, which was attributed to the low bulk density, and it increased sharply as the sintering temperature increasing, just as the curve of the bulk densities of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics with 0.5wt% V_2O_5 addition showed in Fig. 4. The ε_r value of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics with 5wt% V_2O_5 addition reached a constant when the sintering temperature increased to 900°C. The constant ε_r value was 45.8, which was similar to the ε_r value of pure $Ca_2Zn_4Ti_{15}O_{36}$ ceramics sintered at 1170°C. Dielectric constant in composite ceramic can be estimated via the logarithmic mixing rule. The influence from both Zn_2TiO_4 phase and the rutile solid solution phase on the ε_r value of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics was just to keep the ε_r value on a level of 45. The quality factors ($Q \times f$ value) of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics decreased acutely from 21,600 GHz to 13,400 GHz as the content of V_2O_5 addition increasing from 0.0wt% to 5wt%. The contents of Zn_2TiO_4 phase and the rutile solid solution phase increased as the content of V_2O_5 addition increasing. Usually, the increase of secondary phase will increase the dielectric loss and accordingly decrease the Q value of the material, especially the Q value of Zn_2TiO_4 in the microwave range was very low (too low to be measured)[1], which might be responsible for the decrease of the $Q \times f$ value as the content of V_2O_5 addition increasing. The $Q \times f$ value of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics was also influenced by grain size, porosity et al. The $Q \times f$ value of pure $Ca_2Zn_4Ti_{15}O_{36}$ ceramic reached a maximum at the sintering temperature of 1140°C, while the bulk density of pure $Ca_2Zn_4Ti_{15}O_{36}$ ceramic reached a maximum at 1170°C. An abnormal grain growth occurred when the pure $Ca_2Zn_4Ti_{15}O_{36}$ ceramic was sintered at 1170°C (as shown in Fig. 3b), which introduced higher dielectric loss. Thus the $Q \times f$ value of pure $Ca_2Zn_4Ti_{15}O_{36}$ ceramics reached a maximum at 1140°C, which was a little lower than the sintering temperature (1170°C) at which the bulk density reached a maximum. $Ca_2Zn_4Ti_{15}O_{36}$ ceramic with 5wt% V_2O_5 addition that was sintered at 930°C for 2 h exhibits a good microwave dielectric properties of ε_r = 46, $Q \times f$ = 13,400 GHz.

Temperature coefficient of resonant frequency (τ_f value) of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics as a function of the content of V_2O_5 addition was shown in Fig. 6. The temperature coefficient of resonant frequency (τ_f value) of pure $Ca_2Zn_4Ti_{15}O_{36}$ ceramic was 120 ppm/°C, which was similar with that reported by Kim et al. [8]. The τ_f value of

[1] Microwave dielectric properties of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics.

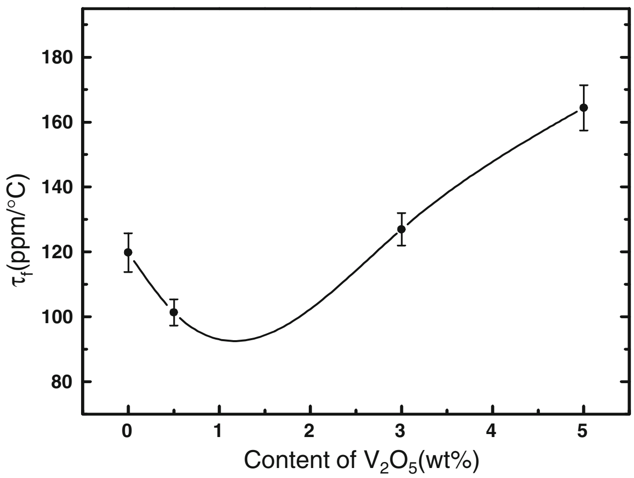

Fig. 6 Temperature coefficient of resonant frequency of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics as a function of the content of V_2O_5 addition

$Ca_2Zn_4Ti_{15}O_{36}$ ceramics changed to +100 ppm/°C when 0.5wt% V_2O_5 was added, while it shifted towards positive as V_2O_5 addition increasing further. The τ_f value of rutile TiO_2 was +465 ppm/°C [14]. Perhaps the τ_f value of the rutile solid solution $(Ca,Zn)_xV_{2x}Ti_{1-3x}O_2$ in present work was also very positive. That might be partially responsible for the results.

4 Conclusions

The crystalline phases, microstructure, sintering behavior and microwave dielectric properties of V_2O_5 doped $Ca_2Zn_4Ti_{15}O_{36}$ ceramics were investigated. The V_2O_5 addition improved the densification and lowered the sintering temperature of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics from 1170 C to 930 C. V_2O_5 reacted with $Ca_2Zn_4Ti_{15}O_{36}$ during the sintering process and the rutile solid solution of $(Ca,Zn)_xV_{2x}Ti_{1-3x}O_2$ might be obtained. The dielectric constant of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics with 0–5wt% V_2O_5 addition were 44–46. The quality factor ($Q \times f$ value) of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics decreased from 21700 GHz to 13400 GHz as the content of V_2O_5 addition increasing from 0 to 5wt%. Temperature coefficients of resonant frequency (τ_f value) of $Ca_2Zn_4Ti_{15}O_{36}$ ceramics changed from 120 ppm/°C to 100 ppm/°C when 0.5wt% V_2O_5 was added and then shifted to positive when the content of V_2O_5 addition increased further. $Ca_2Zn_4Ti_{15}O_{36}$ with 5wt% V_2O_5 addition could be densified well at 930 C and showed a microwave dielectric properties of $\varepsilon_r \approx 46$, $Q \times f \approx 13{,}400$ GHz, $\tau_f \approx +164$ ppm/°C.

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