

Synthesis and characterization of novel $\text{Ca}_2\text{Zn}_4\text{Ti}_{15}\text{O}_{36}$ microwave ceramics derived from sol-gel powder

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Abstract A novel microwave dielectric ceramics with composition of $\text{Ca}_2\text{Zn}_4\text{Ti}_{15}\text{O}_{36}$ (CZT) have been synthesized at different sintering temperatures, using citrate sol-gel derived powder. The sintering behavior and the phase identification of the powders were evaluated using differential thermal analysis-thermo gravimetric analysis and X-ray powder diffraction analysis techniques. The phase of CZT can be observed in the powder calcined at 900 °C. The single-phase of CZT, however, can only be obtained at sintering temperature of 1,000 °C or above. The single-phase CZT ceramics can be sintered into dense at 1,100 °C, exhibiting excellent microwave dielectric properties of $\epsilon_r=48.1$, $Q \times f=27,000$ GHz, and $\tau_f=+53.5$ ppm/°C. The effects of sintering temperature on the density, microstructure, and dielectric properties of the sintered ceramics were investigated. The mechanism responsible for the change of dielectric properties with sintering temperature was also discussed.

Keywords Dielectric properties · Microwave ceramics · Medium permittivity · Sol-gel

1 Introduction

In the past decades, the rapid growth of the wireless communication industry has created a high demand for microwave ceramics components. A variety of microwave devices have been developed using dielectric resonators

(DRs) as the frequency determining components. Most of the commercial DR materials at present are divided into two groups: (1) ceramics with low dielectric constant ($20 < \epsilon_r < 40$) and high Q factor; and (2) ceramics with high dielectric constant (> 65) and low Q factor. Both of these two groups have many available materials. However, materials with dielectric constant in the range 40–65 are few, although such are suitable for the applications requiring both narrow bandwidth and extremely low insertion loss [1]. As part of the drive to develop microwave dielectrics the search for medium permittivity dielectric materials is one of the current areas of research in microwave dielectrics.

Our interest in $\text{Ca}_2\text{Zn}_4\text{Ti}_{15}\text{O}_{36}$ stemmed from recent work investigating phase relations in CaO-ZnO-TiO₂ system. The existence of $\text{Ca}_2\text{Zn}_4\text{Ti}_{15}\text{O}_{36}$ phase was also reported by Kim et al. [2] in their investigating in calcium modified zinc titanates. However, they pointed out that the single-phase $\text{Ca}_2\text{Zn}_4\text{Ti}_{15}\text{O}_{36}$ can not be obtained via solid state reaction method. Thus, it is challenging to achieve single-phase $\text{Ca}_2\text{Zn}_4\text{Ti}_{15}\text{O}_{36}$ ceramics using other methods. In the present paper, we successfully obtained single-phase $\text{Ca}_2\text{Zn}_4\text{Ti}_{15}\text{O}_{36}$ ceramics. The ceramics was prepared using highly reactive powder synthesized by a citrate sol-gel process. The phase formation, sintering behavior, microstructure, and dielectric properties were investigated. It is considered to be a potential candidate for medium permittivity dielectric materials, as well as low temperature-cofired ceramics (LTCC) for microwave applications.

2 Experimental procedure

Microwave dielectric ceramic with a composition of $\text{Ca}_2\text{Zn}_4\text{Ti}_{15}\text{O}_{36}$ (CZT) was synthesized by a citrate sol-gel

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method. High purity $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, butyl titanate ($(\text{C}_4\text{H}_9\text{O})_4\text{Ti}$), and citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) were used as raw materials. Metal nitrates, butyl titanate, and citric acid were dissolved in the deionized water. A small amount of ammonia was added to adjust pH value to about 6. During this process, the mixture was continuously stirred using a magnetic agitator. Heated at about 80 °C for a few hours, the transparent solution was obtained. The solution was then poured into a dish and heated at 110 °C stirring constantly to transform into a xerogel. The xerogel powder was annealed at 1,000 °C to transform into the desired phase.

The synthesized powder was ball-milled in a polyethylene jar for 6 h using zirconia balls in alcohol medium. The milled powders were dried, mixed with an appropriate amount of PVA (5 wt.%) as a binder, granulated, and uniaxially pressed into cylindrical disks of diameter 10 mm and height about 5 mm at a pressure of about 2,000 kg/cm^2 . The specimens were preheated at 600 °C for 2 h to expel the binder and then sintered at temperatures from 1,050 to 1,150 °C for 4 h in air.

The xerogel powder after heated at 250 °C was characterized via thermogravimetric analysis (TGA) and differential thermal analysis (DTA) (SETARAM 92). The crystalline phase of the synthesized powders and sintered specimens were determined by using an X-ray diffractometer with $\text{CuK}\alpha$ radiation (Rigaku D/MAX IIIB, Japan). The bulk densities of the sintered ceramics were measured by Archimedes method. The microstructures of samples were observed by a scanning electron microscope (SEM, JEOL JSM-6301F). The dielectric constant and unloaded quality factor were measured at microwave frequencies in room temperature using the Hakki–Coleman dielectric resonator method and cavity method [3, 4], respectively. The temperature coefficients of resonant frequencies (τ_f) were measured in the temperature range of 25 to 80 °C.

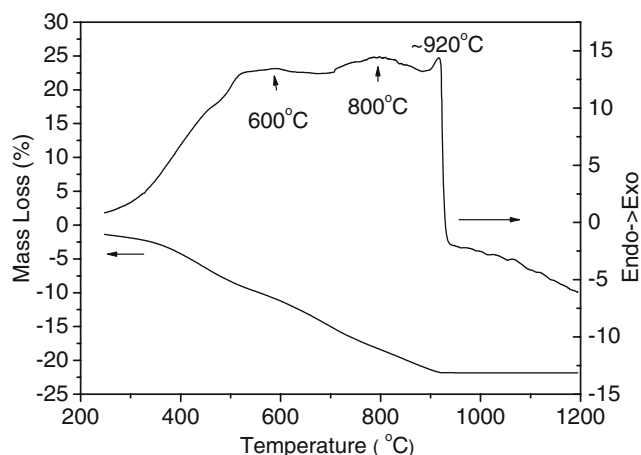


Fig. 1 DTA and TG plots of the xerogel after treated at 250 °C

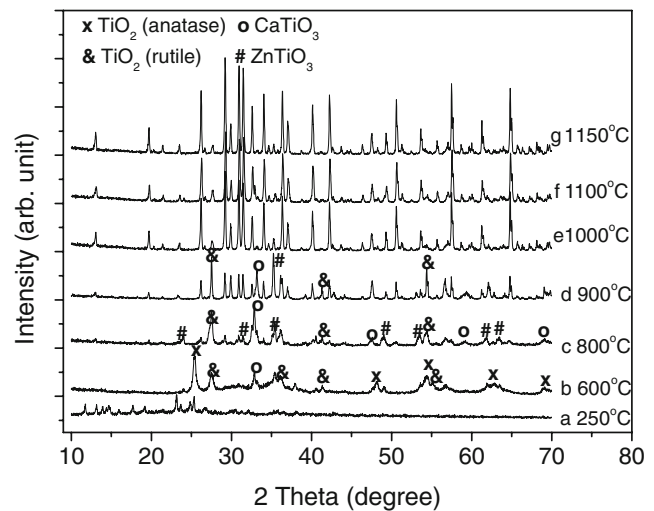


Fig. 2 XRD patterns for the sol-gel powders after calcining at: a 250, b 600, c 800, d 900, e 1,000, f 1,100, and g 1,150 °C

3 Results and discussions

The thermogravimetric analysis and differential thermal analysis were performed at a heating rate of 10 °C/min in static air to characterize the reaction behavior calculated from 250 to 1,200 °C. Before the thermogravimetric analysis and differential thermal analysis, the xerogel was heated at 250 °C to finish a large mass loss due to the autocatalytic anionic oxidation-reduction reaction between the nitrate and citrate systems [5]. This treatment can avoid unwanted extravasation during the analysis process, which makes the measurement on the variation of mass loss at high temperatures more accurate. The typical DTA-TG plot of the treated powders is shown in Fig. 1. It can be seen that a continuous mass loss happened before 920 °C and a series of exothermic reactions occurred. The exothermic peaks are almost overlapped. Fortunately, we can still identify three exothermic peaks at ~600, ~800, and ~920 °C (marked in Fig. 1). The first exothermic peak at ~600 °C may correspond to the decomposition of remaining organics and the formation of new crystalline phase of anatase and rutile. The other two exothermic peaks may correspond to the phase transformation. Mass loss and exothermic reactions stop at temperature above ~930 °C, as illustrated in Fig. 1. These results will be proved by XRD analysis at different temperatures immediately.

Figure 2 shows the XRD patterns of synthesized powders under different temperatures. The XRD patterns were compared with standard data (JCPDS files 21-1272, 21-1276, 26-1500, 42-423, and 34-55). The powder heated at 250 °C remains mainly amorphous in nature. The peaks may correspond to the organics or nitrates, as shown in Fig. 2a. It implies that the formation of the desired crystalline phase is difficult in low sintering temperature conditions, which is similar with that of perovskite structure

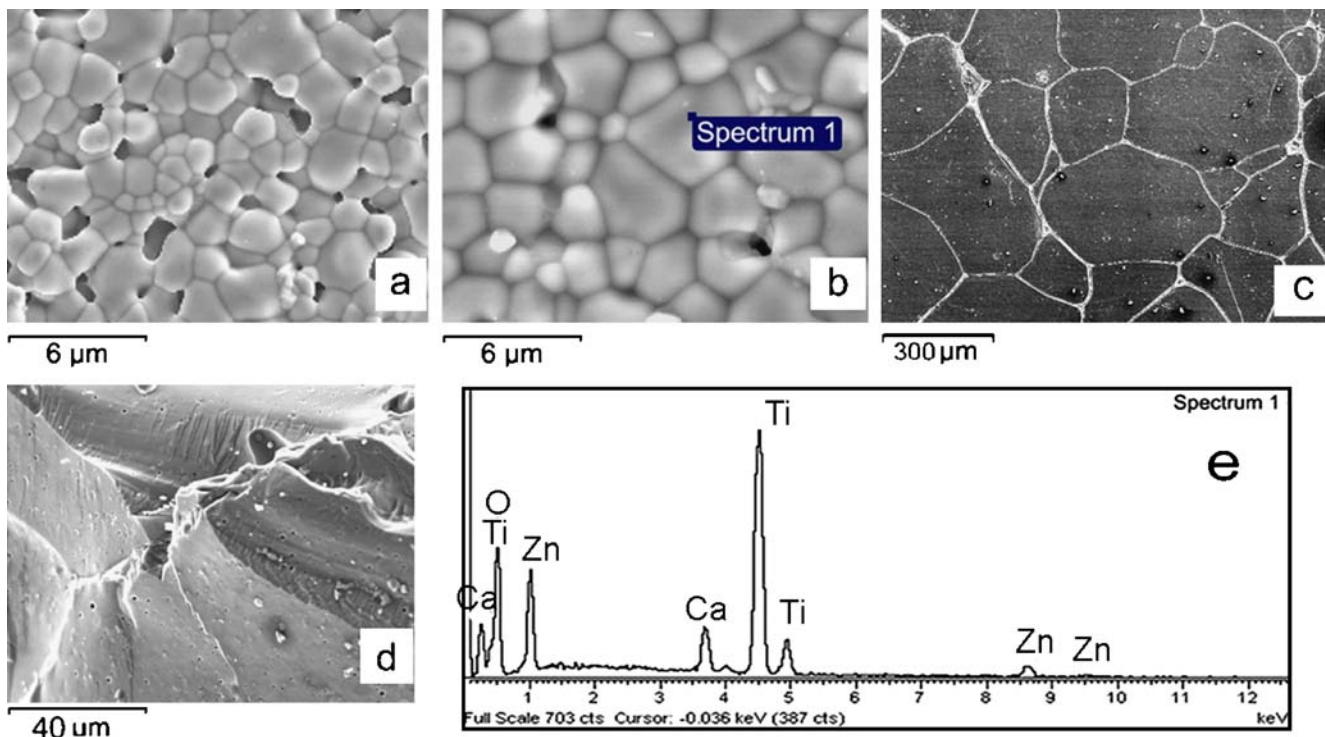


Fig. 3 SEM photographs of surfaces of samples sintered at **a** 1,075, **b** 1,100, **c** 1,150 °C; **d** fractured sections of the sample sintered at 1,150 °C; and **e** composition of sintered sample analyzed by EDX

but different from that of ferrites [6, 7]. However, unlike the formation of the perovskites and ferrites, the CZT phase formed indirectly. In the present case, the TiO_2 of both anatase and rutile phases was formed after annealed at 600 °C. After annealed at 800 °C, the anatase phase disappeared and the CaTiO_3 and ZnTiO_3 phase formed with some residual rutilites, as shown in Fig. 2b and c. It also can be seen that, the XRD peaks of powders annealed at 600 and 800 °C are very broad, reflecting the nano-crystalline nature of the powders. The crystallite size was calculated from full width at half maximum (FWHM) data. The calculated crystallite sizes are about 14 and 19 nm for the powders annealed at 600 and 800 °C, respectively. The phase of CZT was obtained at 900 °C or above, as shown in Fig. 2d–f. The phase analysis was in agreement with the above supposition from DTA-TG results. Single-phase CZT ceramics were successfully synthesized via citrate sol-gel process, which was not achieved via a traditional solid-state reaction method [2]. It is believed that the incomplete reactions are owing to the lack of homogeneity and activity of the reactants. In the present case, citrate sol-gel process was performed, guaranteeing the molecular blend and small particle size. Thus, complete reaction and single-phase CZT compounds were achieved owing to the high homogeneity and high reactivity of the sol-gel derived powders.

The microstructures of sintered ceramics were observed by using scanning electron microscopy. The typical SEM images of CZT ceramics sintered at different temperatures

are shown in Fig. 3. With the increase of sintering temperature, the grain size increased rapidly. The samples sintered at 1,075 °C have an average grain size of ~ 2 μm , whereas samples sintered at 1,100 and 1,150 °C have an average grain size of ~ 4 and ~ 350 μm , respectively. Dense and uniform ceramics can be prepared at 1,100 °C, whereas an abrupt grain growth happened at about 1,150 °C. The abrupt grain growth was considered to be owing to the formation of liquid phase during the sintering process. Moreover, the porosity was also observed in the fractured section of the sample sintered at 1,150 °C, as shown in Fig. 3d. In order to identify the composition of the sample, the EDX analysis was performed on the surface of the samples. Several grains were detected and the typical results are shown in Fig. 3e. The atomic percentages of calcium, zinc, and titanium ions are 3.16, 6.29, and 24.12%, which

Table 1 Density and microwave dielectric properties of $\text{Ca}_2\text{Zn}_4\text{Ti}_{15}\text{O}_{36}$ ceramics.

S.T.(°C)	Relative density (%)	ϵ_r	$Q \times f$ (GHz)	τ_f (ppm/°C)
1,050	88.6	37.8	12,700	+52.2
1,075	95.6	45.9	18,500	+58.5
1,100	98.5	48.1	27,000	+53.5
1,125	98.6	48.1	26,000	+47.3
1,150	98.5	48.4	25,500	+46.8

are in agreement with the stoichiometry of the title compound. This experiment implies that, though citrate sol-gel route, very dense ceramics with single-phase of CZT can be obtained at 1,100 °C, which are in agreement with the results of XRD analysis.

The bulk density and dielectric properties of ceramics at microwave frequencies, corresponding to different sintering temperatures, are summarized in Table 1. It can be seen that the bulk density increases with increasing sintering temperature and remains a saturated value of about 4.170 g/cm³ at 1,100 °C and above, which is near the theoretical density of the title compound. Both of the dielectric constant and the $Q \times f$ value increased with increasing sintering temperature from 1,050 to 1,100 °C, owing to the density increase and grain growth. For samples sintered from 1,100 to 1,150 °C, the dielectric constant slightly increased from 48.1 to 48.4 and the $Q \times f$ value slightly dropped from 27,000 to 25,500 GHz. These results were also attributing to the grain growth and the porosity in the microstructure. As it is known, the increase of grain size has a positive effect on the dielectric constant and $Q \times f$ value, whereas that of the porosity in the microstructure is negative. For the ceramics sintered below 1,100 °C, with increase of sintering temperature, the grain size increased and the porosity decreased. Thus, the integrative effect on the dielectric properties is positive. The dielectric constant and the $Q \times f$ value increased significantly with sintering temperature. Further increase of sintering temperature above 1,100 °C cause rapid grain growth, but the porosity may also increase during the process. These two opposite effect may counteract the effect on the dielectric properties. However, for all sintered temperature ranges, all prepared ceramics exhibit positive τ_f value of about +50 ppm/°C. The τ_f value is not much affected by the sintering temperature. As it is known, the τ_f value is related to the composition and the secondary phase of a material. Thus, the present results imply that no composition or phase changes happened from 1,050 to 1,150 °C.

In view of the present results, it is believed that by suitable doping, substitution or by additives, one can easily tune the dielectric properties or sintering temperatures. Thus, this ceramic exhibited great potential for developing

the medium-permittivity dielectric materials, as well as LTCC materials for microwave applications.

4 Conclusions

Highly homogeneous and high reactive ceramic powder with composition of Ca₂Zn₄Ti₁₅O₃₆ was synthesized via citrate sol-gel process. Microwave dielectric ceramics were prepared at different sintering temperatures using the synthesized powder. The phase of CZT was transformed from the reaction between CaTiO₃, ZnTiO₃ and TiO₂. Single-phase CZT can be achieved at 1,000 °C or above. At 1,100 °C, very dense ceramics with uniform grains and fine dielectric properties with a dielectric constant of 48.1, $Q \times f$ value of 27,000 (at 6.5 GHz), and τ_f value of +53.5 ppm/°C were achieved. The sintering temperature significantly affects the bulk density, microstructure, and dielectric properties of the sintered ceramics. The dependence of dielectric constant and $Q \times f$ value on the sintering temperature was associated with the variation of microstructure, which were largely depend on the sintering temperature. This ceramic is believed to be a potential candidate for the medium permittivity dielectric materials and LTCC materials for microwave applications.

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References

1. W. Wersing, *Curr. Opin. Solid State Mater. Sci.* **1**, 715 (1996)
2. H.T. Kim, J.D. Byun, Y. Kim, *Mater. Res. Bull.* **33**, 963 (1998)
3. B.W. Hakki, P.D. Coleman, *IRE Trans. Microwave Theor. Tech.* **MMT-8**, 402 (1960)
4. W.E. Courtney, *IEEE Trans. Microwave Theor. Tech.* **MMT-18**, 476 (1970)
5. Z. Yue, J. Zhou, X. Wang, Z. Gui, L. Li, *J. Eur. Ceram. Soc.* **23**, 189 (2003)
6. Z. Yue, L. Li, J. Zhou, H. Zhang, Z. Gui, *Mater. Sci. Eng., B* **64**, 68 (1999)
7. Z. Yue, Y. Zhang, Z. Gui, L. Li, *Appl. Phys., A* **80**, 1757 (2005)