

# A novel microwave dielectric ceramic $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$ : Preparation and dielectric properties

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## Abstract

A novel microwave dielectric powder with composition of  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  was synthesized through a citrate sol–gel process. The development of crystalline phases with heat-treating temperature for the gel derived powders was evaluated by using thermo-gravimetric analysis and X-ray powder diffraction analysis techniques. The pure phase of  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  with crichtonite crystal structure was obtained at relatively low temperature of 1000 °C. The synthesized powder has high reactivity and the dense ceramics with single crystalline phase were obtained at low sintering temperature of 1100 °C. Impedance spectroscopy and microwave dielectric measurements on sintered samples showed the present compound to be a modest dielectric insulator with excellent dielectric properties of  $\epsilon_r \sim 47\text{--}49$ ,  $Q$  factor  $\sim 27,800\text{--}31,600$  GHz and  $\tau_f \sim +45$  to  $+50$  ppm/°C. It shows comparable microwave dielectric properties to other moderate-permittivity microwave dielectrics, but much lower sintering temperature of 1100 °C.

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**Keywords:** Microwave dielectric ceramics; Dielectric properties; Sol–gel process;  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  compound

## 1. Introduction

In the past decades, the rapid growth of the wireless communication industry has created a high demand for microwave ceramic components. A variety of microwave devices have been developed using dielectric resonators (DRs) as the frequency determining components. DRs provide a compact, low-cost, and highly reliable choice as resonator elements in microwave circuits. Due to the constraints of size, frequency of operation, frequency stability, and selectivity, only those materials with high dielectric constant, low dielectric loss (i.e. high  $Q$  factor) and low temperature coefficient of resonant frequency meet the requirements for DR applications [1].

The commercial microwave dielectric ceramics available are divided into two groups: (i) ceramics with low dielectric constant ( $20 < \epsilon_r < 40$ ) and high  $Q$  factor, which are used for DRs; and (ii) ceramics with high dielectric constant ( $> 65$ ) and relatively low  $Q$  factor, which are mainly used

for dielectric filters. Both of these two groups have many available materials, such as  $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ ,  $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$  [2–4],  $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  [5],  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  [6,7],  $(\text{Zr}, \text{Sn})\text{TiO}_4$  [8,9] for the former, and tungsten–bronze-type materials in the  $\text{BaO}\text{--}\text{Re}_2\text{O}_3\text{--}\text{TiO}_2$  system [10] and perovskite materials in  $\text{CaO}\text{--}\text{Li}_2\text{O}\text{--}\text{Re}_2\text{O}_3\text{--}\text{TiO}_2$  system [11,12] for the latter. However, materials with dielectric constant in the range from 40 to 65 are few, although such are suitable for the applications requiring both narrow bandwidth and extremely low insertion loss [1], for instance, base station resonator applications. As part of the drive to develop microwave dielectrics the search for moderate permittivity dielectric materials is one of the current areas of research in microwave dielectrics.

Our interest in  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  stemmed from recent work investigating phase relations in the  $\text{CaO}\text{--}\text{ZnO}\text{--}\text{TiO}_2$  system. This compound belongs to crichtonite structural series, having general formula  $AM_{21}\text{O}_{38}$ , where  $A$ - and  $M$ -sites are occupied by large and small cations, respectively [13]. As far as we are aware, little attention has been paid to the possible use of crichtonite-related compounds as microwave dielectric materials. The crichtonite-structure

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is based on a nine-layer close-packed anion lattice in which the *A*- and *M*-cations occupy 12-coordinated and 8- or 6-coordinated positions, respectively [14,15]. A similar compound of stoichiometry  $\text{Ca}_2\text{Zn}_4\text{Ti}_{15}\text{O}_{36}$  has been recently reported by Kim et al. [16] in their investigation on calcium modified zinc titanates, which was the first report of the microwave dielectric properties of crichtonite-related compounds. However, they pointed out that the single-phase  $\text{Ca}_2\text{Zn}_4\text{Ti}_{15}\text{O}_{36}$  cannot be obtained via solid-state reaction method. As we all know, the solid-state synthesis has several inherent disadvantages, viz., inhomogeneous and incomplete redox reaction is more common during the fabrication of the complex mixed oxide phases like this case. Solution chemistry route-like co-precipitation, combustion or sol-gel provide an intimate blending of the constituents in the synthesis of these materials. Therefore, the phase pure materials with improved powder characteristics, for example, smaller particle size, higher surface area and better sinterability can be achieved. These processes are of significance for preparation of electroceramics with less impurity phases.

In this paper, we report the well sintered, single-phase  $\text{Ca}_2\text{Zn}_4\text{Ti}_{15}\text{O}_{38}$  ceramics using highly reactive powder synthesized by a citric sol-gel process. Dense ceramics can be obtained at about 1100 °C. The crystal structures, microstructures, electrical and dielectric properties of the ceramics were investigated. It is considered to be a potential candidate for moderate permittivity dielectric materials for microwave applications.

## 2. Experimental procedure

Microwave dielectric ceramics with a composition of  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  was synthesized by a citrate sol-gel 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, which could form 30 g of ceramic powder, were dissolved in 400 ml of 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 gel powder was then heat-treated at 1000 °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 1 or 5 mm at a pressure of about 2000 kg/cm<sup>2</sup>. The samples were preheated at 600 °C for 2 h to expel the binder and then sintered at temperatures from 1050 to 1150 °C for 4 h in air and then annealed at 1000 °C for 6 h in oxygen atmosphere to eliminate unexpected impurities.

Electrodes for capacitance and impedance spectroscopy measurements were fabricated from silver paste, which were fired in air at 800 °C for 30 min to decompose the paste and harden the residue.

The crystal structure of the powders and sintered pellets was determined by using an X-ray diffractometer with  $\text{CuK}\alpha$  radiation (Rigaku D/MAX IIB, Japan). Data were collected over the  $2\theta$  range 10–80°, with a step width of 0.02° and count-time of 4 s per step. The bulk densities of the sintered ceramics were measured by Archimedes method. The microstructures of samples were observed by a scanning electron microscope (JEOL JSM-6301F, Japan). The stoichiometry of the samples was measured using the SEM/EDX facility with Oxford ISIS software. The electrical and dielectric properties at low frequencies were measured from a combination of fixed frequency (1 kHz, 1 MHz) capacitance measurements at 1 V using an LCR meter (HP 4284A, Japan), and impedance spectroscopy over a frequency range from 40 Hz to 15 MHz at 100 mV from 25 to 800 °C using an impedance analyzer (Agilent 4294A, Japan). Samples were loaded into a conductivity jig and placed in a horizontal tube furnace controlled to  $\pm 1$  °C. The relative permittivity and dielectric loss at microwave frequencies were characterized at room temperature by the Hakki-Coleman DR method and cavity method [17,18] using a network analyzer (HP 8720ES, USA). The temperature coefficients of resonant frequencies ( $\tau_f$ ) were measured in the temperature range of 25–80 °C.

## 3. Results and discussions

Large weight loss usually occurred when heat-treating the precursors, due to the decomposition and combustion of the organic reagents used in the citrate sol-gel method. Fig. 1 shows the typical TGA curve (solid line) for the  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  precursor heated in static air at a heating rate of 10 °C/min. Almost 60% of the initial weight is lost below 400 °C with a further loss of 20% between 400 and 600 °C. Above 600 °C only a small amount of residual losses are observed. This implies that the decomposition of the organic products and the subsequent combustion have finished at that temperature. The dash line is the derivative of the weight loss curve, from which the rate of weight loss was evaluated, as shown in Fig. 1. The first peak at 193 °C corresponds to the combustion process in which an autocatalytic anionic oxidation-reduction reaction between the nitrates and citrates takes place, as reported in other nitrate-citrate gel system [19]. Peaks at 340, 489, 595 and 758 °C may be caused by the decomposition and combustion reactions of the excessive carboxyl groups and residual carbon formed from the oxidation-reduction reaction.

In order to identify the formation process of crystal phases, portions of the powders were calcined at different temperatures and then characterized by X-ray powder diffraction. Fig. 2 shows the evolution of phases with

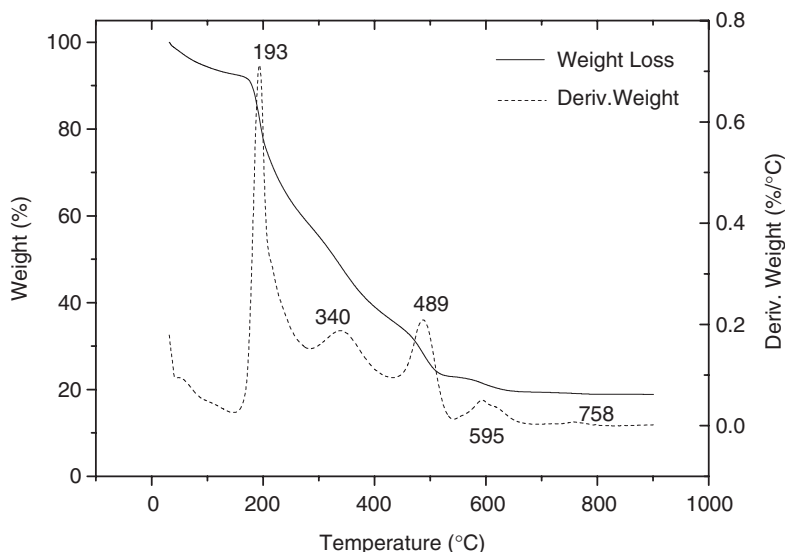
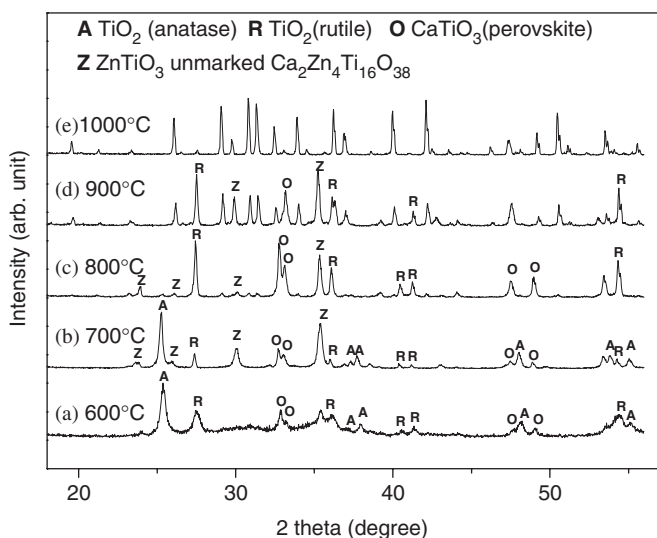


Fig. 1. TGA curve of the dried gel precursor.

Fig. 2. XRD patterns for the  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  precursor powders after calcining at: (a) 600 °C, (b) 700 °C, (c) 800 °C, (d) 900 °C, and (e) 1000 °C.

temperature for the synthesized powders. The  $\text{TiO}_2$  of both anatase and rutile phases and  $\text{CaTiO}_3$  with perovskite structure were formed after heat-treated at 600 °C. In addition, the diffraction peaks are noticeably broadened, implying the nano-crystalline nature of the powders. At 700 °C, a new phase of  $\text{ZnTiO}_3$  was observed. For the powders annealed at 800 °C, most of anatase phase transformed into rutile phase with increasing intensities of perovskite phase peaks. In fact, the presence of  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  phase could also be noticed at this temperature, though its reflections are weak. With further increase of temperature, the reflections of  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  phase significantly increase, and all the intermediate phases disappear after heat-treated at 1000 °C for 4 h. The present experiment indicated that single-phase  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$

ceramics could be successfully synthesized via the citrate sol-gel process, which was not achieved via a traditional solid-state reaction method due to the lack of homogeneity and activity of the reactants [16]. In the present case, the homogeneous blending in atomic scale and the resultant nanocrystalline particles with high reactivity derived from the citrate sol-gel process are responsible for the formation of the single-phase compound.

Fig. 3 shows the X-ray diffraction (XRD) patterns for the  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  powder obtained with calcination temperature of 1100 °C (4 h in air) and annealing temperature of 1000 °C (6 h in  $\text{O}_2$ ). The XRD patterns were fully indexed using the published data [20] of rhombohedral space group  $R\bar{3}$  with  $a = 9.198 \text{ \AA}$  and  $\alpha = 68.67^\circ$  (or  $a_{\text{H}} = 10.376 \text{ \AA}$ ,  $c_{\text{H}} = 20.95 \text{ \AA}$ ). The results are in good agreement with that reported previously [20] and confirmed the powder to be phase-pure. The compound of  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  was firstly reported by Gatehouse and Grey [20]. Fig. 4 shows the crystal structure of this compound represented on the basis of their previous report for ease of expression. The compound of  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  is iso-structural with crichtonite-related compounds, having a structure based on an anion framework with one large calcium cation per unit cell occupying an anion site. The closest-packed anion layers have a nine-layer stacking sequence ...ABCBCACABA..., i.e. (hhcc...). Within a unit cell, one large calcium cation occupied at anion site with coordination number of 12, and two zinc cations occupied at tetrahedral site with coordination number of 4. The other cations, including one calcium cation, two zinc cations, and all 16 titanium cations located between the anion layers occupying octahedral sites with coordination number of 6. From the polyhedral point of view, the cations with coordination number of 6 ( $\text{Ti}^{4+}/\text{Zn}^{2+}/\text{Ca}^{2+}$ ) formed octahedra, which represent both corner- and edge-sharing octahedra, as shown in Fig. 4. These octahedral

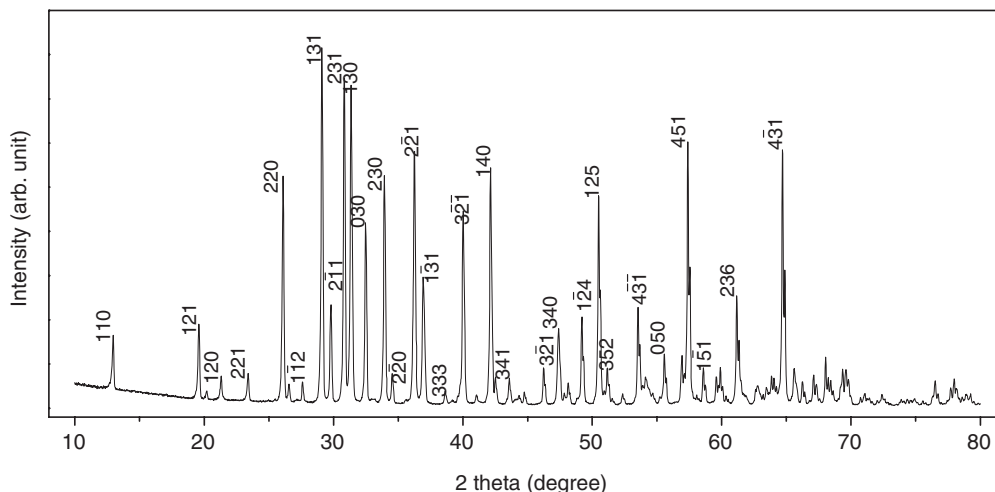


Fig. 3. X-ray diffraction patterns of  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  powder sintered at  $1100^\circ\text{C}$  for 4 h in air and annealed at  $1000^\circ\text{C}$  for 6 h in oxygen atmosphere.

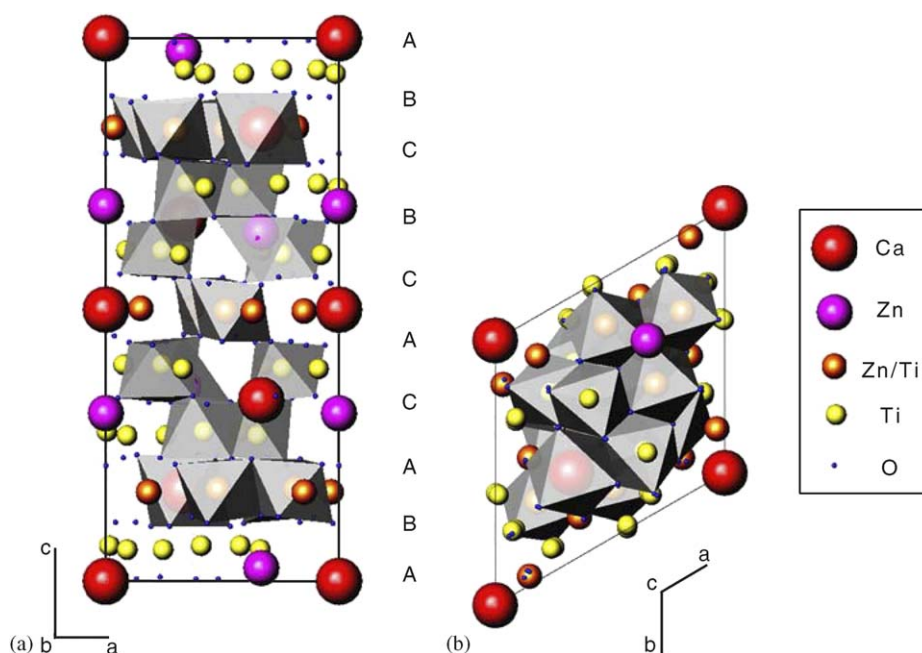


Fig. 4. Schematic structural models of hexagonal unit cell for  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  viewed along  $b$ -axis (a) and  $c$ -axis (b). The crystal structure model was built on the basis of Ref. [20] reported by B.M. Gatehouse and I.E. Grey in 1983.

connection manners were considered to affect the dielectric properties of this compound and it would be discussed later. The more detailed information about the structure refinement of  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  is reported in Ref. [20].

The bulk densities of the pellets were obtained by Archimedes method. The relative density increased from 89.3% to 98.4% on increasing the temperature from 1050 to  $1150^\circ\text{C}$  (Table 1). This suggested that gel-derived powder was reactive enough to be sintered into a dense body at  $1100^\circ\text{C}$  or above. The microstructures of sintered ceramics were observed by using scanning electron microscopy (SEM). The typical SEM images of dense  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  ceramics are shown in Fig. 5a. It illustrates that

dense and uniform ceramics with isotropic grains were obtained for samples sintered at  $1100^\circ\text{C}$  for 4 h in air and annealed at  $1000^\circ\text{C}$  for 6 h in oxygen atmosphere. An average grain size of about  $5\text{--}6\ \mu\text{m}$  was observed for this case. This experiment indicates that, though citrate sol-gel route, very dense ceramics with single-phase of  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  can be obtained at  $1100^\circ\text{C}$ . In addition, it was reported [21,22] that the evaporation of ZnO during the sintering process was inevitable for high-temperature sintered Zn-containing dielectric ceramics (i.e.  $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ , etc.). The most obvious effects of ZnO loss are the occurrence of Zn vacancies and the appearance of impurity phases. Thus, the dielectric properties would be

Table 1  
Bulk densities and microwave dielectric properties of  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  ceramics sintered at different temperatures

Sintering condition <sup>a</sup>	Density (%)	$\epsilon_r$	$Qf$ (GHz)	$f$ (GHz)	$\tau_f$ (ppm/°C)
1050 °C (4 h/air)	89.3	40.6	24,900	7.137	58
1075 °C (4 h/air)	97.3	47.5	29,100	6.425	50
1100 °C (4 h/air)	98.4	48.4	31,600	6.667	48
1150 °C (4 h/air)	98.3	48.5	27,800	6.517	49

<sup>a</sup>All samples were annealed at 1000 °C for 6 h in oxygen atmosphere.

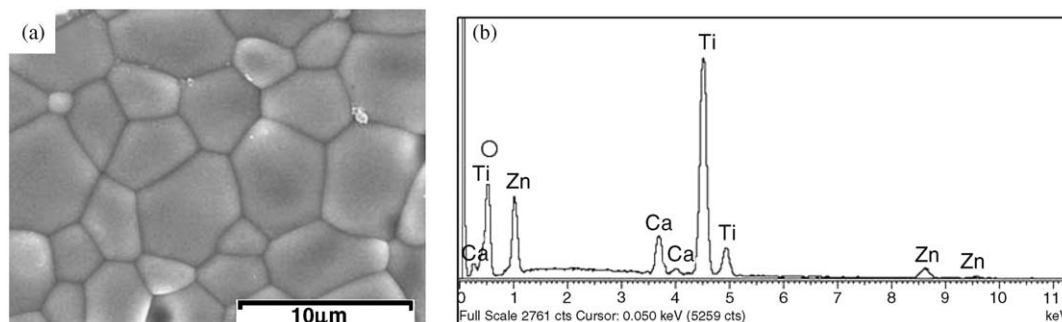


Fig. 5. Scanning electron micrograph of  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  ceramics sintered at 1100 °C for 4 h in air and then annealed at 1000 °C for 6 h (a), and typical EDX analysis results (b).

affected. On the other hand, ZnO-loss was not expressly mentioned in the reports of those low-temperature sintered Zn-containing materials (i.e.  $\text{ZnTiO}_3$ ,  $\text{ZnNb}_2\text{O}_6$ , etc. [23–25]), implying that the effect of zinc volatilization could be ignored when sintering temperature was below 1150 °C. In order to identify the homogeneity and composition of the sintered ceramics, the energy-dispersive X-ray (EDX) analysis was performed on the surface of the samples. The X-ray images were observed and the samples were proved to be homogeneous of each element. The composition was obtained on the basis of the quantitative EDX analysis performed on several grains. The typical results are shown in Fig. 5b and the atomic percentages of calcium, zinc, and titanium ions are 3.27%, 6.45%, and 26.03%, respectively. It is well in agreement with the stoichiometric composition of  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  that the deviation from stoichiometric composition was observed to be less than 4%. Such a small deviation from the desired stoichiometric composition of  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  was considered to be beneficial from the decrease in the evaporation of ZnO during the sintering process due to the low sintering temperature. This result was consistent with the previous reports in other low-temperature sintered Zn-containing ceramic systems [23–25].

The electrical measurements were carried out on the dense ceramics sintered at 1100 °C in air and then annealed at 1000 °C in oxygen atmosphere. The ceramics were too resistive ( $>10^7 \Omega \text{cm}$ ) to measure by impedance spectroscopy at room temperature. Thus, the impedance measurement at elevated temperatures was performed. The complex planes ( $Z^*$ ) of impedance data collected at 600 °C were plotted in Fig. 6. Single semi-circular arc was

obtained at different measurement temperatures, indicating that an equivalent circuit consisting of a single parallel RC element can be modeled. The small feature at low frequencies in the  $Z^*$  plot shown in Fig. 6a is associated with an electrode effect. The associated capacitance of the arcs were calculated from the relationship  $R\omega C = 1$  at  $Z''_{\text{max}}$  (where  $\omega = 2\pi f$  and  $f$  is the applied frequency). The capacitance of the sample is about 4–4.8 pF/cm, indicating a bulk response with a permittivity of about 45–55. The electrical homogeneity of the ceramics was confirmed by the presence of single, Debye-like peaks occurring at similar frequencies in spectroscopic plots of the imaginary components of the impedance ( $Z''$ ) and electric modulus ( $M''$ ), as shown in Fig. 6b. The bulk resistivity at elevated temperatures was calculated from the intercept of the arc on the real axis at low frequencies in  $Z^*$  plots. An Arrhenius plot of bulk conductivity,  $\sigma$  (where  $\sigma = 1/R$ ) is shown in Fig. 7. It shows good linearity over the measured temperature range, with an activation energy ( $E_a$ ) of  $\sim 1.33 \text{ eV}$ . The linear Arrhenius-type response indicates that the conducting mechanism may be a simple band-gap model at elevated temperatures. Based on the approximation that the intrinsic band gap,  $E_g \sim 2E_a$ , the intrinsic conduction associated with ionization of carriers from the valence band to the conduction band with a band gap of  $> 2.66 \text{ eV}$ .

The dielectric characterization at low frequencies was performed on the dense ceramics sintered at 1100 °C in air and then annealed at 1000 °C in oxygen atmosphere. The dielectric constants at 1 kHz and 1 MHz of the sample were 51.5 and 50.8, respectively. Microwave dielectric resonance measurements at room temperature showed samples to

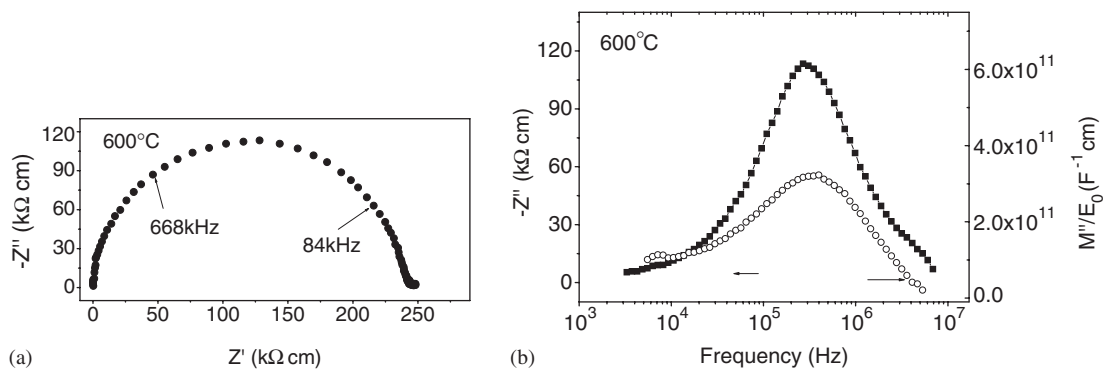


Fig. 6.  $Z^*$  plot (a) and combined  $-Z''$ ,  $M''$  spectroscopic plot (b) for  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  ceramics at  $600^\circ\text{C}$ .

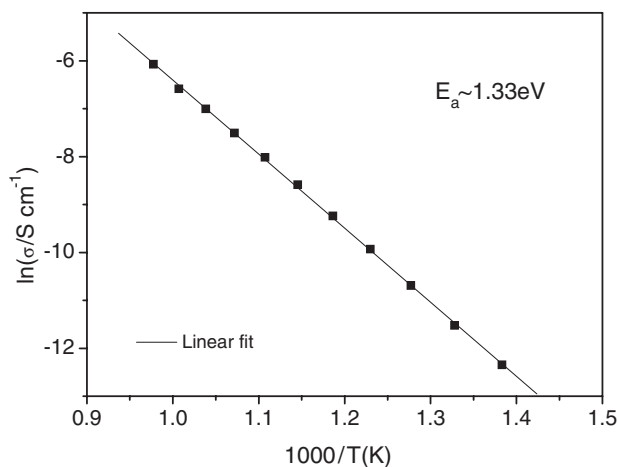


Fig. 7. Arrhenius plot of bulk conductivity versus temperature for  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  ceramics sintered at  $1100^\circ\text{C}$  in air and annealed at  $1000^\circ\text{C}$  in oxygen atmosphere.

resonate at  $f \sim 6\text{--}7\text{ GHz}$ , with  $\epsilon_r \sim 47\text{--}49$  and  $Qf$  value  $\sim 27,800\text{--}31,600\text{ GHz}$  for all ceramics with  $>90\%$  density, and the temperature coefficient of resonant frequency,  $\tau_f$  was about  $+45$  to  $+50\text{ ppm}/^\circ\text{C}$  for both samples, as listed in Table 1. It is also clear that the sintering processing did not have a dramatic influence on the microwave dielectric properties for the samples with  $>90\%$  density.

From the dielectric measurements, the present compound shows a moderate permittivity with rather low dielectric loss at microwave frequency. The moderate permittivity was considered to be related to the crystal structure, especially to the octahedral connection manners of the oxygen. Generally speaking, octahedral connections of oxygen mainly influence the effective ion polarization of dielectrics. Among the three octahedral connections of oxygen, face-sharing corresponds to the smallest polarization, edge-sharing is larger, and corner-sharing corresponds to the largest. As we know, rutile phase  $\text{TiO}_2$  and perovskite  $\text{CaTiO}_3$ , with only corner-sharing octahedra of  $\text{Ti-O}_6$ , show dielectric constant of 104 and 162, respectively [26,27]. For moderate dielectrics compounds, such as  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  and  $(\text{Zr}_{1-x}\text{Sn}_x)\text{TiO}_4$ , the  $\text{Ti-O}_6$  octahedra usually share both edges and corners with each other

[7,9].  $\text{ZnTiO}_3$  and  $\text{MgTiO}_3$  with ilmenite structure have small dielectric constant of about 20, which are owing to the presence of certain amount of face-sharing  $\text{Ti-O}_6$  octahedra in the ilmenite structure [28,29]. As discussed above, the  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  compound has only corner- and edge-sharing octahedra, similar with those of  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  and  $(\text{Zr}_{1-x}\text{Sn}_x)\text{TiO}_4$ . The present dielectric measurement results were exactly in agreement with the above analysis.

In view of the present results, the  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  ceramics has a higher dielectric constant than that of  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  or  $(\text{Zr}_{1-x}\text{Sn}_x)\text{TiO}_4$ , and the dielectric loss is low enough for practical application. It is also comparable to the recently developed moderate permittivity dielectrics, such as  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  with  $\epsilon_r \sim 43$ ,  $Qf$  value  $\sim 16,000\text{ GHz}$  and  $\tau_f \sim -17\text{ ppm}/^\circ\text{C}$ ,  $\text{CaLa}_4\text{Ti}_4\text{O}_{15}$  with  $\epsilon_r \sim 45$ ,  $Qf$  value  $\sim 35,000\text{ GHz}$  and  $\tau_f \sim -25\text{ ppm}/^\circ\text{C}$ , or  $\text{Ca}_2\text{La}_4\text{Ti}_5\text{O}_{18}$  with  $\epsilon_r \sim 49$ ,  $Qf$  value  $\sim 20,000\text{ GHz}$  and  $\tau_f \sim 6\text{ ppm}/^\circ\text{C}$  [30,31]. Comparing with those moderate-permittivity dielectrics, the present compound can be sintered into dense at much lower temperatures. Unfortunately, the temperature coefficient of resonant frequency of the  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  ceramic is a bit larger, which maybe the only weakness of this compound.

#### 4. Conclusions

Novel microwave dielectrics with composition of  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  have been prepared by a citrate sol-gel process. The crichtonite-related phase,  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  compound was achieved after complete reactions between  $\text{CaTiO}_3$ ,  $\text{TiO}_2$  and  $\text{ZnTiO}_3$ , which were the fine-mixed resultants of organic gel precursors with small particle size. The well-sintered powders were confirmed to be single-phase of  $\text{Ca}_2\text{Zn}_4\text{Ti}_{16}\text{O}_{38}$  on the basis of powder XRD and SEM-EDX analysis results. Dense ceramics can be obtained after sintering at  $1100^\circ\text{C}$  or higher. Comparing with other published moderate microwave dielectrics, the present compound has much lower sintering temperatures of  $1100^\circ\text{C}$  and comparable properties of  $\epsilon_r \sim 47\text{--}49$ ,  $Qf$  value  $\sim 27,800\text{--}31,600\text{ GHz}$  and  $\tau_f \sim +45$  to  $+50\text{ ppm}/^\circ\text{C}$ .

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