

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 value $\sim 27,800\text{--}31,600$ 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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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/cm². 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 2θ 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 ± 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 (τ_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

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