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Synthesis and microwave dielectric properties of $CaSiO_3$ nanopowder by the sol–gel process

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Abstract

The synthesis and microwave dielectric properties of $CaSiO_3$ nanopowder by sol–gel method have been investigated in this paper. $CaSiO_3$ nanoparticles with an average grain size of 50–60 nm were obtained by calcining the CaO–SiO_2 xerogel that was prepared from Calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) and tetraethylortho silicate (TEOS). Calcining the CaO–SiO_2 xerogel at 1150 °C, the pseudowollastonite-$CaSiO_3$ phase was completely formed. However, the main phase is not $CaSiO_3$ or $CaSi_2O_4$ but SiO_2 when calcining the mixture of SiO_2 and $CaCO_3$ at 1150 °C. Comparing with CaO–SiO_2 ceramics prepared by solid-state process, the $CaSiO_3$ ceramics made from nanopowders calcined at 1000 °C achieved more compact structure at the sintering temperature of 1320 °C, and then had excellent microwave dielectric properties: $\varepsilon_r = 6.69$, $Qf = 25398$ GHz.

Keywords: $CaSiO_3$; Sol–gel; Microwave dielectric ceramic; Nanopowder

1. Introduction

Wollastonite ($CaSiO_3$) is a mineral that has many uses in numerous branches of national economies over the world and can be used for the production of special radio ceramics, sanitary components, porcelain materials, lining bricks, glaze and flux [1]. At 1125 °C, the Wollastonite-$CaSiO_3$ will transform into pseudowollastonite-$CaSiO_3$ ceramic. $CaSiO_3$ ceramics are also used as a biomaterial in medical industry for artificial bone and dental root because it showed good bioactivity and biocompatibility [2–4].

$CaSiO_3$ ceramics possess excellent dielectric properties: $\varepsilon_r = 5$, $tg\delta = (1.0\text{–}3.0) \times 10^{-4}$ [5]. However, the sintering temperature range of pure $CaSiO_3$ is very narrow and the sample becomes more porous with increasing the calcination temperature [6]. So it is difficult to obtain dense $CaSiO_3$ ceramics materials by the traditional solid-state preparation process. In order to improve the sintering characteristic, the study on the synthesis of CaO–B_2O_3–SiO_2 (CBS) glass–ceramics and decreasing sintering temperature with aids have been investigated. Cai et al. reported that the excessive SiO_2 and clay can reduce the sintering temperature (1170–1230 °C) of $CaSiO_3$, and the dielectric properties are: $\varepsilon_r = 7.0\text{–}9.0$, $tg\delta = (1.0\text{–}5.0) \times 10^{-4}$ [5]. Chang et al. demonstrated that the dielectric properties of the CBS system which comprised of $CaSiO_3$, $Ca_6Si_4O_3$ and CaB_2O_4 are: $\varepsilon_r = 5.1$, $tg\delta = 0.0013$ (1 GHz) [7,8].

Sol–gel processing has been used for the fabrication of ceramic materials with improved compositional homogeneity and with lower densification temperatures [9]. The advantages of wet chemical routes arise from the careful control of composition, which can be effected by mixing the constituents at a molecular level in solution. The sol–gel method is with the advantages of the chemical route of a lower annealing temperature in the crystallization process and the crystal growth of particles is easier to be controlled by varying the heat treatment [10]. The gelation process of the CaO–SiO_2 system and its mechanism has been investigated, and $CaSiO_3$ powder with an average grain size of 0.2–1.4 um was obtained by sol–gel method and ion exchange [11–13]. However, the study on preparation and dielectric properties of $CaSiO_3$ nanoparticles has not been reported.

In this paper, the $CaSiO_3$ nanoparticles were low-temperature synthesized by the sol–gel method and the influence factors

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of gelation were well controlled in the process. The thermal decomposition behavior of gel precursor was examined, and the structure, size, sintering and microwave dielectric properties of the bulks made from the nanopowders were characterized.

2. Experimental procedure

For the typical experimental procedure to prepare $CaSiO_3$ nanoparticles, Calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) was dissolved in deionized water and ethanol, and Tetraethylortho silicate (TEOS) was dissolved into ethanol first. Two solutions were mixed and stirred for 2 h at room temperature to form a mix solution with the molar ratio of Calcium nitrate tetrahydrate to Tetraethylortho silicate was 1:1. With constant stirring, an appropriate amount of HNO_3, CH_3COOH, H_2O and PEG2000 as dispersant were slowly added into this mixed solution until a transparent green sol was obtained. The sol was held at 60 °C until a transparent gel was formed. Then, the transparent gel was poured into a dish and dried at 90 °C for 24 h to transform into dried gel. The dried gels were calcined at 800–1150 °C for 1 h with a heating rate of 5 °C min^{-1} to eliminate organic content and obtained CaO–SiO_2 powders. 8 wt.% PVA was added into the nanopowders calcined at 1000 °C, and then the powders were pressed into pellets with 18 mm in diameter and 9 mm in thickness under a uniaxial pressure of 1350 kgf cm^{-2}. The pellets were subsequently sintered for 2 h in air from 1260 to 1340 °C.

The thermal decomposition behavior of the gels was examined by a thermoagravimetric analyzer (TG, WRT-3P) at a heating rate of 10 °C min^{-1} and a differential thermal analyzer (DTA, CRT-2) in air. The crystalline phases of the calcined particles were identified by an X-ray diffractometer (Rigaku D/Max-RA) with Cu Kα radiation (36 kV, 30 mA, $2\theta = 10°–80°$). The grain sizes of powders were observed by scanning electron microscopy (SEM, S-571, Hitachi) and transmission electron microscopy (TEM, JEM-1230). The density of sintered bulks was measured by Archimedean method. The surface morphology of bulks made from nanopowders was examined by scanning electron microscopy. Microwave dielectric constants ε_r and the quality values *Qf* at microwave frequencies were measured by Hakki-Coleman dielectric resonator method using an Agilent 8719ET (50 MHz to 13.5 GHz) Network Analyzer.

3. Results and discussion

Fig. 1 shows the differential thermal analysis (DTA) and thermogravimetric (TG) analysis for CaO–SiO_2 dried gel. Corresponding to the first weight loss shown by TG (the temperature ranges from room temperature to 530 °C), the endothermic peak in the DTA curve around 132 °C is due to the volatilizations of the solvent (ethanol) and water, and the exothermic curve ascending slowly around 200–530 °C is owing to the decomposition of organic species. The largest endothermic peak around 579 °C, accompanied by another sharp weight loss, is due to the decomposition of nitrate. The endothermic peak around 661 °C corresponding to a rapid weight loss is associated with the decomposition of $CaCO_3$. The TG curve shows that there is no obvious weight change when the temperature is higher than 800 °C, and the corresponding slow ascending exothermic curve in DTA is due to the gradual formation of the $CaSi_2O_4$ and $CaSiO_3$ crystalline phases that was confirmed by XRD.

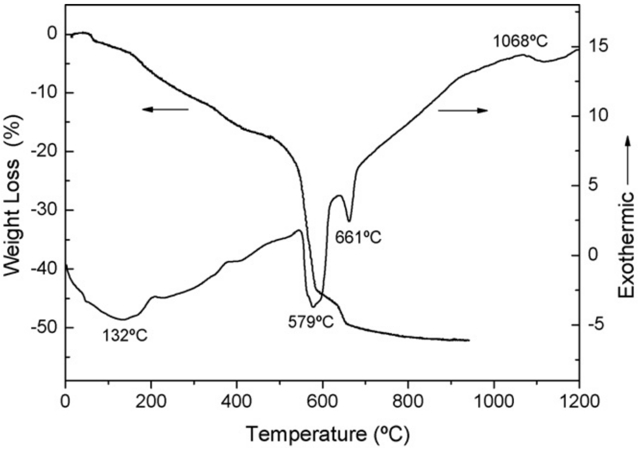

Fig. 1. TG and DTA curves for CaO–SiO_2 dried gels.

Fig. 2 shows the X-ray diffraction patterns (XRD) of CaO–SiO_2 powders calcined at different temperatures for 1 h. At 800 °C, Larnite-Ca_2SiO_4 and CaO were observed. When the calcination temperature increased to 900 °C, there were four phases: Calcium silicate-$CaSiO_3$, Larnite-Ca_2SiO_4, Wollastonite-$CaSiO_3$ and SiO_2. The presence of Wollastonite-$CaSiO_3$ as the main crystalline phase was observed at 1000 °C, in association with Larnite-Ca_2SiO_4 and SiO_2 and pseudowollastonite-$CaSiO_3$ as minor phases. At 1150 °C, the pseudowollastonite-$CaSiO_3$ phase was completely formed. However, the mixture of SiO_2 and $CaCO_3$ calcined at 1150 °C by the solid-state process, the main phase is not $CaSiO_3$ or $CaSi_2O_4$ but SiO_2. It indicates that the powder prepared by sol–gel method achieved single $CaSiO_3$ more easily than that by solid-state preparation process.

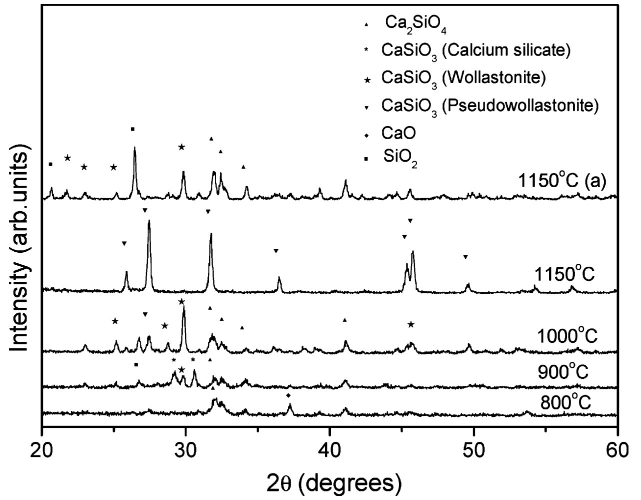

Fig. 2. XRD patterns of CaO–SiO_2 powders calcined at different temperatures. (a) By solid-state process.

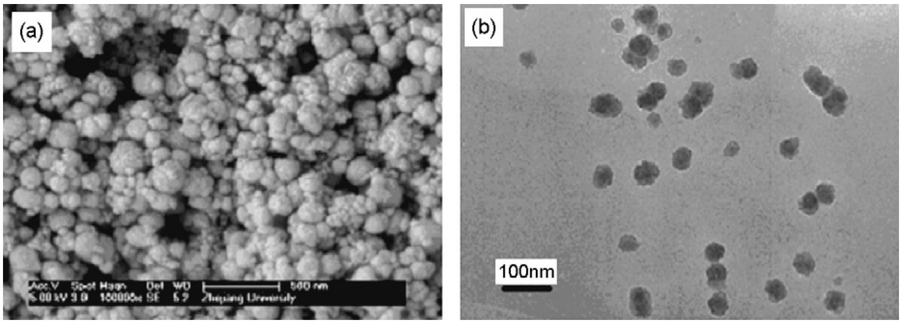

Fig. 3. Micrographs of the $CaO–SiO_2$ powders calcined at 1000 °C. (a) SEM photograph, (b) TEM photograph.

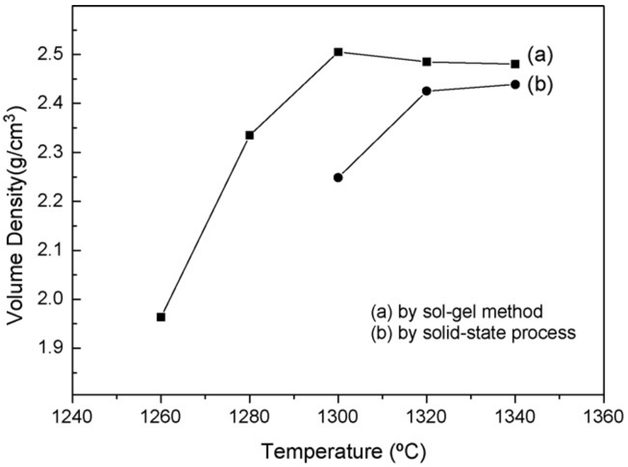

Fig. 4. Bulk densities of $CaO–SiO_2$ as a function of sintering temperature.

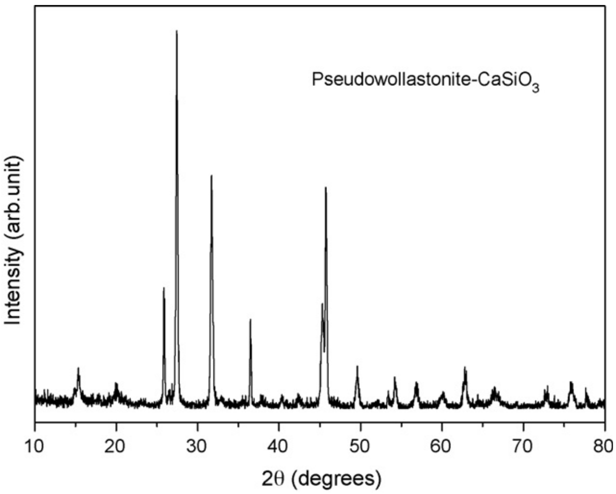

Fig. 5. XRD pattern of pellet sintered at 1320 °C from powder prepared by sol–gel method.

The scanning electron micrograph (SEM) and transmission electron micrograph (TEM) of the $CaO–SiO_2$ powders calcined at 1000 °C are indicated in Fig. 3. From the SEM photograph, it was observed that the average particle size in diameter was about 50–60 nm and many of these particles were agglomerated to spheroid with a size of 100–200 nm. When dispersed in ethanol by ultrasonic, the particles showed narrow size distributions and highly dispersed, which can be seen in TEM photograph.

Curve (a) of Fig. 4 shows the bulk densities of the $CaO–SiO_2$ nanoparticles sintered at different temperatures. The density value increased from 1.964 to 2.505 g cm^{-3} as the sintering temperature was raised from 1260 to 1300 °C and then changed little with increasing the sintering temperature. In contrast to that, the maximum bulk density value of the $CaO–SiO_2$ ceramic prepared by the conventional solid process is only 2.439 g cm^{-3} with increasing the sintering temperature from 1300 to 1340 °C, which is shown in curve (b). These results suggest that the $CaO–SiO_2$ nanoparticles with large specific surface area were sufficient to promote the sintering process.

The XRD pattern and SEM photographs of the $CaO–SiO_2$ ceramics are shown in Figs. 5 and 6, respectively. At the sintering temperature of 1320 °C, the single-phase pseudo-wollastonite-$CaSiO_3$ was observed (PDF # 740874). From the

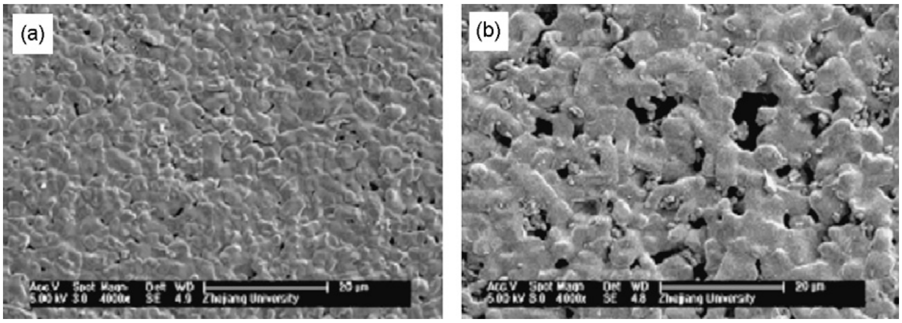

Fig. 6. SEM photographs of $CaO–SiO_2$ pellets sintered at 1320 °C. (a) By sol–gel method, (b) by solid-state process.

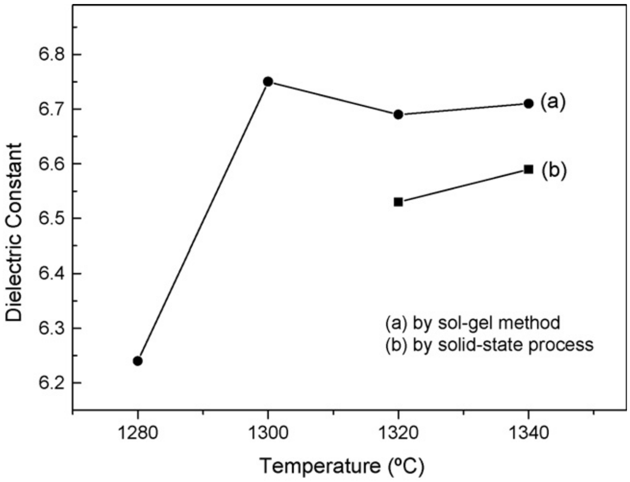

Fig. 7. Dielectric constants of pellets as a function of sintering temperature.

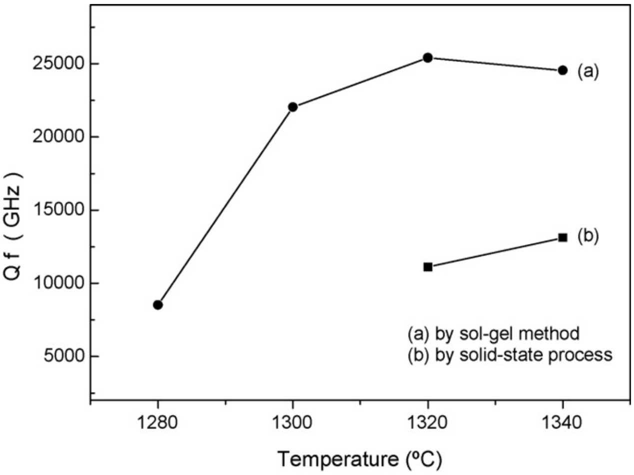

Fig. 8. *Qf* values of pellets as a function of sintering temperature.

micrographs, it is clear that the sample sintered at 1320 °C had low porosity and the grains were uniform by sol–gel method which is shown in Fig. 6(a). However, using solid-state process, as shown in Fig. 6(b), the sintered sample was porous and the grains were larger than that in Fig. 6(a). These results suggest that the CaO–SiO_2 nanoparticles can observably improve the compactness of CaO–SiO_2 ceramic.

Figs. 7 and 8 illustrate the dielectric constant and *Qf* value of the samples sintered at different temperatures. It is noticed that microwave dielectric properties of the samples closely correspond to bulk density of the samples. The dielectric constant and *Qf* value increased with sintering temperature due to the increase of densities and then saturated. Comparing to the solid-state ($\varepsilon_r = 6.59$, $Qf = 13109$ GHz, at 1340 °C), the $CaSiO_3$ ceramic made from nanopowder prepared by sol–gel method had better properties ($\varepsilon_r = 6.69$, $Qf = 25398$ GHz, at 1320 °C) is attributed to the better $CaSiO_3$ microstructure, as confirmed in Fig. 6.

4. Conclusions

$CaSiO_3$ nanoparticles with an average grain size of 50–60 nm have been synthesized by the sol–gel method. Compared with the conventional solid-state reaction method, the sol–gel process showed good stoichiometric control and achieved the single-phase $CaSiO_3$ powders at a relatively low temperature (less than 1150 °C). The sintering characteristic, microstructure and dielectric properties of $CaSiO_3$ ceramics had been obviously improved for the nanoeffect. At the sintering temperature of 1320 °C, the $CaSiO_3$ ceramics made from nanopowders prepared by sol–gel method achieved excellent dielectric properties: $\varepsilon_r = 6.69$, $Qf = 25398$ GHz.

Acknowledgments

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