Study of 0.9Al$_2$O$_3$–0.1TiO$_2$ ceramics prepared by a novel DCC-HVCI method

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Study of $0.9\text{Al}_2\text{O}_3-0.1\text{TiO}_2$ ceramics prepared by a novel DCC-HVCI method

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Abstract: In this paper, in-situ coagulation of 0.9Al₂O₃–0.1TiO₂ suspension and microwave dielectric properties of 0.9Al₂O₃–0.1TiO₂ ceramics prepared by a novel direct coagulation casting via high valence counter ions (DCC-HVCI) method were proposed. The 0.9Al₂O₃–0.1TiO₂ suspension could be coagulated via controlled release of calcium ions from calcium iodate at an elevated temperature. The influence of tri-ammonium citrate (TAC) content, solid loading, and calcium iodate content on the rheological properties of the suspension was investigated. In addition, the influence of coagulation temperature on coagulation time and properties of green bodies was also studied. It was found that the stable 0.9Al₂O₃–0.1TiO₂ suspension could be successfully prepared by adding 0.3 wt% TAC and adjusting pH value to 10–12 at room temperature. 0.9Al₂O₃–0.1TiO₂ green bodies with uniform microstructures were coagulated by adding 8.0 g/L calcium iodate after treating at 70 °C for 1 h. 0.9Al₂O₃–0.1TiO₂ ceramics, sintered at 1500 °C for 4 h and annealed at 1100 °C for 5 h, showed uniform microstructures with density of 3.62±0.02 g/cm³. The microwave dielectric properties of 0.9Al₂O₃–0.1TiO₂ ceramics prepared by DCC-HVCI method were: $\varepsilon_r = 11.26\pm0.06$, $Q\times f = 11569\pm629$ GHz, $\tau_f = 0.93\pm0.60$ ppm/°C. The DCC-HVCI method is a novel and promising route without binder removal process to prepare complex-shaped microwave dielectric ceramics with uniform microstructures and good microwave dielectric properties.

Keywords: rheological properties; microwave dielectric properties; 0.9Al₂O₃–0.1TiO₂; DCC-HVCI

1 Introduction

With the rapid development of microwave communication technology, the demand of microwave dielectric ceramics with low dielectric constant ($\varepsilon_r$), high quality factor ($Q\times f$), and near-zero temperature coefficient of resonator frequency ($\tau_f$) is rising [1]. Al₂O₃ ceramics have been widely applied in many fields like circuit board, dielectric resonators, and patch antennas due to their high quality factor (500,000 GHz) and relative low dielectric constant ($\varepsilon_r = 10$) [2–4]. However, the application of Al₂O₃ ceramics was limited by high $\tau_f$ (~60 ppm/°C) and sintering temperature (~1600 °C) [5]. TiO₂, on the contrary, has positive $\tau_f$ value, so a near-zero $\tau_f$ could be...
achieved by adding a certain amount of TiO$_2$ to Al$_2$O$_3$ [6]. Ohishi et al. [7] and Miyauchi et al. [8] found 0.9Al$_2$O$_3$–0.1TiO$_2$ ceramics had a near-zero $\tau_f$, while a detrimental Al$_2$TiO$_5$ secondary phase could form during the sintering process, which could decrease the quality factor of ceramics. It was reported that annealing treatment is an effective way to eliminate Al$_2$TiO$_5$ secondary phase. Ohishi et al. [7] reported good dielectric properties of 0.9Al$_2$O$_3$–0.1TiO$_2$ ceramics with $\varepsilon_r = 12.4$, $Q\times f = 117000$ GHz, $\tau_f = +1.5$ ppm/°C after annealing at 1000 °C for 2 h. In addition, Miyauchi et al. [8] obtained a higher dielectric property of 0.9Al$_2$O$_3$–0.1TiO$_2$ ceramics with $\varepsilon_r = 12.4$, $Q\times f = 148000$ GHz, $\tau_f = +1.5$ ppm/°C after annealing at 1100 °C.

At present, 0.9Al$_2$O$_3$–0.1TiO$_2$ ceramics have been mostly prepared by dry-pressing, but this method cannot prepare ceramics with complex shapes and uniform microstructures, which significantly restricts the application of 0.9Al$_2$O$_3$–0.1TiO$_2$ ceramics. Nevertheless, gel-casting technique could prepare complex-shaped ceramics with high performance by in-situ coagulation of ceramic suspension [9–12]. Wu et al. [13] systematically studied microwave dielectric properties of 0.9Al$_2$O$_3$–0.1TiO$_2$ ceramics prepared by gel-casting. Compared with dry-pressing method, gel-casting technique could effectively improve the performance of microwave dielectric ceramics. However, neurotoxicity of acrylamide monomer used in gel-casting process cannot be ignored. Furthermore, long-time binder removal process also limits its application to some extent [14,15].

Direct coagulation casting (DCC), which introduces Derjaguin–Landau–Verwey–Overbeek (DLVO) theory into colloidal forming technique [16], could be used to prepare complex-shaped ceramics without binder removal process. Suspension coagulates by either adjusting its pH value to isoelectric point or increasing the ionic intensity [17,18]. However, long coagulation time and low strength of green body hindered its application to some extent [19,20]. Recently, a new colloidal forming technique, which is called direct coagulation casting via high valence counter ions (DCC-HVCI) based on DLVO theory and Schulze–Hardy electrostatic valence rule [21–23], has attracted attention of researchers [24–29]. Chen et al. [24,25] and Xu et al. [26–29] used calcium iodate, calcium phosphate, calcium citrate, magnesium citrate, and magnesium oxide as sources of high valence counter ions to compress the electrical double-layer and realize in-situ coagulation of ceramic suspension, respectively. The DCC-HVCI method, with short coagulation time, high strength of green body (~3 MPa), and no binder removal process, has been successfully used to prepare the structural ceramics. However, so far, it has been rarely reported to prepare microwave dielectric ceramics by DCC-HVCI method.

In this paper, DCC-HVCI method was used to prepare 0.9Al$_2$O$_3$–0.1TiO$_2$ microwave dielectric ceramics. Tri-ammonium citrate (TAC) was used as dispersant to prepare 0.9Al$_2$O$_3$–0.1TiO$_2$ suspension with high solid loading and low viscosity. The calcium ions released from calcium iodate was used for the in-situ coagulation of 0.9Al$_2$O$_3$–0.1TiO$_2$ suspension. The influence of dispersant content, solid loading, and calcium iodate content on the rheological properties of the 0.9Al$_2$O$_3$–0.1TiO$_2$ suspension was investigated. Additionally, the effect of coagulation temperature on coagulation time and properties of green body was studied. Finally, the microstructures, phase compositions, and microwave dielectric properties of 0.9Al$_2$O$_3$–0.1TiO$_2$ ceramics were investigated.

## 2 Experimental procedure

### 2.1 Raw materials

Commercial available Al$_2$O$_3$ powders (Almatis, Ludwigshafen, Germany) with average particle size of 0.33 µm and TiO$_2$ powders (Aladdin, Shanghai, China) with average particle size of 0.92 µm were used as raw materials to prepare the 0.9Al$_2$O$_3$–0.1TiO$_2$ powders. The microstructures of Al$_2$O$_3$ and TiO$_2$ powders are shown in Figs. 1(a) and 1(b). The 0.9Al$_2$O$_3$–0.1TiO$_2$ powders were prepared by solid-state reaction method [13]. Figure 1(c) shows the microstructure of prepared 0.9Al$_2$O$_3$–0.1TiO$_2$ powders and Fig. 1(d) shows the EDS image of Ti distributing uniformly in 0.9Al$_2$O$_3$–0.1TiO$_2$ powders. TAC was used as dispersant to prepare negatively charged suspension. Ammonia was used to tailor the pH of the suspension. Analytical reagent grade calcium iodate (Ca(IO$_3$)$_2$·6H$_2$O) was used as the source of high valence counter ions Ca$^{2+}$. TAC, ammonia, and calcium iodate were all purchased from Sinopharm Chemical Reagent Co., Ltd., China. Deionized water was used in all preparation process.
2.2 Suspension preparation and coagulation process

Figure 2 shows the flowchart of experimental processes. 0.9Al2O3–0.1TiO2 suspension was prepared by milling the 0.9Al2O3–0.1TiO2 powders, TAC, ammonia, and deionized water in a polyamides jar with zirconia grinding media in a planetary ball mill for 1 h. The mass ratio between grinding media and 0.9Al2O3–0.1TiO2 powders was 4:1. When the 0.9Al2O3–0.1TiO2 suspension was preserved and cooled down at 10 °C in a refrigerator for 4 h, calcium iodate powders were added to the suspension and the milling process was continued for another 5 min. After degassing in vacuum condition for 15–20 min, the suspension was cast into several plastic molds, which were heated in a water bath at different temperatures for a period of time, and then demolded to make green bodies. The green bodies were then dried at 80 °C in a drying oven for 24 h and sintered at 1500 °C for 4 h at a heating rate of 3 °C/min, followed by annealing at 1100 °C for 5 h in air.

2.3 Characterization

Microstructures of samples were characterized by a scanning electron microscope (SEM, JSM-7600F, JEOL, Japan) coupled with an energy dispersive spectroscopy (EDS). The zeta potential of 0.9Al2O3–0.1TiO2 suspension was measured by a zeta potential analyzer (CD-7020, Colloidal Dynamics, USA) via the electroacoustic measurement technique with a stirring speed of 300 r/min. The solid loading of the suspension was 10 vol%. The rheological properties of the suspension were measured by a Discovery DHR-2 rheometer (TA Instrument, New Castle, USA). The density of the sintered samples was measured by Archimedes method. Phase compositions of the sintered 0.9Al2O3–0.1TiO2 ceramics were determined by X-ray diffraction using Cu Kα radiation (XRD-7000s, Japan) from 10° to 80° with a scanning speed of 10 (°)/min. The dielectric constant (\(\varepsilon_r\)) and \(Q\timesf\) values were
measured in the TE_{011} mode with the Hakki and Coleman’s method [30] using a vector network analyzer (Advantest R3767C, Advantest Corporation, Tokyo, Japan) and parallel silver boards. The temperature coefficient of resonant frequency (\( \tau_f \)) was calculated by the following formula:

\[
\tau_f = \frac{1}{f(25)} \times \frac{f(75) - f(25)}{75 - 25}
\]

where \( f(25) \) and \( f(75) \) represent the resonant frequency at 25 °C and 75 °C, respectively.

3 Results and discussion

3.1 Preparation of 0.9Al_2O_3–0.1TiO_2 suspension

As is known, high solid loading and low viscosity ceramic suspension is necessary for direct coagulation casting process. TAC exhibits good dispersing stability and is one of the most widely used dispersants, especially for alumina and other oxide ceramic powders [31]. Figure 3 shows the zeta potential of 10 vol% 0.9Al_2O_3–0.1TiO_2 suspension at different pH values. Without TAC, the isoelectric point of 0.9Al_2O_3–0.1TiO_2 suspension is around 6. Relatively high zeta potential is achieved when pH is in the range of 10–12, so a stable negatively charged suspension can be prepared due to the absorption of OH\(^{-}\) on the surface of 0.9Al_2O_3–0.1TiO_2 particles. By adding TAC, zeta potential remains in the negative region and no isoelectric point occurs in this test. The absolute value of zeta potential increases with the increase of pH and achieves the highest value when pH = 12, so a stable negatively charged suspension could be received because of the absorption of citrate ions on the surface of 0.9Al_2O_3–0.1TiO_2 particles. The results above indicates that TAC improves the repulsive force between 0.9Al_2O_3–0.1TiO_2 particles, which is beneficial to the stable dispersion of the particles in the alkaline region. Therefore, the well-dispersed 0.9Al_2O_3–0.1TiO_2 suspension could be prepared with the addition of TAC at the pH of 10–12.

Figure 4 shows the effect of TAC contents on the rheological properties of 25 vol% 0.9Al_2O_3–0.1TiO_2 suspension. The viscosities of 0.9Al_2O_3–0.1TiO_2 suspension with different contents of TAC exhibit a shear thinning behavior, which is a typical non-Newtonian fluid, so the consequent degassing process would not increase the viscosity of the suspension. The inserted image in Fig. 4 shows that the curves of adding 0.25 wt% and 0.5 wt% TAC almost overlap, while the viscosity of the suspension dispersed by adding more than 0.75 wt% TAC increases distinctly. With the increase of TAC amount, the citrate ion contents absorbed on the surface of 0.9Al_2O_3–0.1TiO_2 particles increase, that is, the stability of the suspension increases. When the TAC amount exceeds 0.75 wt%, redundant citrate ions cause the increase of ion intensity, which could compress the electrical double-layer and decrease the electrostatic repulsion. In macroscopic point of view, the viscosity of 0.9Al_2O_3–0.1TiO_2 suspension increases. Hence, the proper dispersant content to prepare stable 0.9Al_2O_3–0.1TiO_2 suspension is in the range of 0.25–0.75 wt%. In this case, 0.3 wt% TAC is used in the subsequent experiments.

Suspension with high solid loading and low viscosity is necessary for colloidal forming method to obtain desirable green bodies with low shrinkage and high dimensional accuracy, which contributes to the
performance of final ceramic products. The relation between relative viscosity (\(\eta_r\)) and solid loading (\(\phi\)) is commonly simulated by Dougherty–Krieger (D–K) model for monodispersed suspensions as following [32]:

\[
\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{\frac{m}{m}} \eta
\]

where \(\phi_m\) is the maximum packing fraction, and \([\eta]\) is the intrinsic viscosity. \(\phi_m\) and \([\eta]\) are used to fit the experimental results and analyze the suspension structure. Figure 5 shows the relative viscosities of 0.9Al\(_2\)O\(_3\)–0.1TiO\(_2\) suspensions with different solid loadings at a shear rate of 100 s\(^{-1}\). The simulated relative viscosity can be expressed as

\[
\eta_r = \left(1 - \frac{\phi}{0.702}\right)^{-7.101+0.702}
\]

It is found that the relative viscosity of the suspension increases with the increase of solid loading. The viscosity of the suspension increases slightly when solid loading is less than 50 vol\%, while the relative viscosity increases dramatically from 536.4 to 2036.5 when the solid loading increases from 50 to 55 vol\%, which causes difficulty in preparing 0.9Al\(_2\)O\(_3\)–0.1TiO\(_2\) suspension. Therefore, 0.9Al\(_2\)O\(_3\)–0.1TiO\(_2\) suspension with solid loading of 50 vol\% is selected.

### 3.2 Coagulation of 0.9Al\(_2\)O\(_3\)–0.1TiO\(_2\) suspension

As is well known, temperature control is mostly applied to the DCC-HVCI technique because many systems are sensitive to temperature [33]. Calcium iodate is an inorganic salt and can be slightly soluble in water at room temperature; however, the solubility increases obviously at an elevated temperature [28]. The forming process in this paper is achieved by releasing Ca\(^{2+}\) from calcium iodate with increasing temperature. The absorption of citrate ions (C\(_6\)H\(_5\)O\(_7\))\(^{3–}\) from ionized TAC on the surface of 0.9Al\(_2\)O\(_3\)–0.1TiO\(_2\) particles results in intense electrostatic repulsion and thus, stable dispersion of the suspension can be achieved. The dissolution reaction can be expressed as

\[
\text{Ca}[\text{IO}_3]_2 \rightarrow \text{Ca}^{2+} + 2\text{IO}_3^{-}
\]

Ca\(^{2+}\) has opposite charge to C\(_6\)H\(_5\)O\(_7\))\(^{3–}\) that could adsorb on 0.9Al\(_2\)O\(_3\)–0.1TiO\(_2\) particle surface, so the electrical double-layer is compressed and the electrostatic repulsion decreases, which causes the decrease of suspension stability. Furthermore, Ca\(^{2+}\) could react with C\(_6\)H\(_5\)O\(_7\))\(^{3–}\) and form calcium citrate, which is insoluble in water and promotes the precipitation of the suspension.

\[
3\text{Ca}^{2+} + 2\text{C}_6\text{H}_5\text{O}_7^{3–} \rightarrow \text{Ca}_3(\text{C}_6\text{H}_5\text{O}_2)_2 \downarrow
\]

Figure 6 shows the effect of calcium iodate concentration on the viscosity of 50 vol\% 0.9Al\(_2\)O\(_3\)–0.1TiO\(_2\) suspension at 25 °C. The viscosity of the suspension increases slightly when the calcium iodate concentration is less than 8.0 g/L, and the viscosity is far below 1 Pa·s which could meet the colloidal processing requirements [28]. However, an abrupt increase of viscosity occurs when the calcium iodate concentration is higher than 8.0 g/L. The viscosity of the suspension comes to 3.0 Pa·s when the concentration of calcium iodate is 8.5 g/L, which is a high viscosity value to transform the suspension from liquid to solid state. As a result, 8.0 g/L calcium iodate is used in the following experiments.

Table 1 shows the coagulation time and state of green bodies prepared by DCC-HVCI method at different coagulation temperature. It is found that the coagulation time decreases with the increase of coagulation temperature. When the coagulation temperature is
Table 1  Coagulation time and state of green bodies prepared by DCC-HVCI method at different coagulation temperature

| Coagulation temperature (℃) | Coagulation time (min) | State of the green body |
|-----------------------------|------------------------|-------------------------|
| 25                          | > 360                  | Cracking                |
| 40                          | 150                    | Cracking                |
| 55                          | 90                     | Flawless                |
| 70                          | 60                     | Flawless                |
| 85                          | 40                     | Cracking                |

relatively low (25℃ and 40℃), calcium iodate can hardly dissolve so that the content of high valence counter ions of Ca²⁺ and the ability to compress the electrical double-layer are limited, which results in a long coagulation time (more than 150 min). In this situation, cracks are observed in green bodies due to inhomogeneous coagulation process. However, when the coagulation temperature is relatively high (55℃ and 70℃), the high valence counter ions of Ca²⁺ release properly with the increase of solubility of calcium iodate and effectively compress the electrical double-layer of dispersed particles. Uniform and flawless wet-coagulated bodies are obtained with relatively short coagulation time (60–90 min). When the coagulation temperature reaches 85℃, water in the 0.9Al₂O₃–0.1TiO₂ suspension evaporates shortly, that is, the coagulation of the suspension is mostly due to the evaporation of water instead of the effect of compressing the electrical double-layer. Green body still cracks even though the coagulation time is short (40 min). From the above, the wet-coagulated body obtained from the 0.9Al₂O₃–0.1TiO₂ suspension after treating at 70℃ presents a homogeneous composition without cracking and possesses the relatively short coagulation time of 60 min. Therefore, the coagulation temperature of 70℃ is chosen for the direct coagulation casting.

3.3 Properties of green bodies and 0.9Al₂O₃–0.1TiO₂ ceramics

Figure 7 shows the photograph and microstructure of green bodies prepared by DCC-HVCI method. Complex-shaped samples with flawless surface are successfully prepared (see Fig. 7(a)). Figure 7(b) shows a uniform microstructure of green body prepared by this method, which is helpful for the mass transfer in the sintering process and beneficial for the properties of the final 0.9Al₂O₃–0.1TiO₂ ceramics.

Figure 8 shows the XRD patterns of different 0.9Al₂O₃–0.1TiO₂ ceramic samples. There are Al₂O₃, TiO₂, and Al₂TiO₅ phases in 0.9Al₂O₃–0.1TiO₂ ceramics after sintering at 1500℃ for 4 h (see Fig. 8(b)). Ohishi et al. [7] announced that Al₂TiO₅ tends to decompose to Al₂O₃ and TiO₂ in the temperature range of 1000–1200℃ due to its low thermal stability. As shown in Fig. 8(a), after annealing treatment, there are only Al₂O₃ and TiO₂ phases existing in the ceramics, while the peak intensities of Al₂O₃ and TiO₂ phases increase due to the decomposition of Al₂TiO₅. The XRD patterns show that the annealing treatment has successfully eliminated the Al₂TiO₅ secondary phase, which ensures good microwave dielectric properties of 0.9Al₂O₃–0.1TiO₂ ceramics. Figure 9 shows the microstructure of 0.9Al₂O₃–0.1TiO₂ ceramics sintered at 1500℃ for 4 h and annealed at 1100℃ for 5 h. No obvious pores and uniform microstructures have been observed in the 0.9Al₂O₃–0.1TiO₂ ceramics prepared by DCC-HVCI method, which is benifical for improving properties of the ceramics.

The density of the 0.9Al₂O₃–0.1TiO₂ ceramics prepared by DCC-HVCI method is 3.62±0.02 g/cm³ and the microwave dielectric properties of 0.9Al₂O₃–0.1TiO₂...
ceramics prepared by DCC-HVCI method are \( \varepsilon_r = 11.26\pm0.06, \ Q \times f = 11569\pm629 \ \text{GHz}, \ \tau_f = 0.93\pm0.60 \ \text{ppm/}^\circ\text{C}. \) The good properties of 0.9Al\(_2\)O\(_3\)–0.1TiO\(_2\) microwave dielectric ceramics are obtained due to the elimination of the Al\(_2\)TiO\(_5\) secondary phase by annealing treatment and uniform microstructure. In the process of DCC-HVCI, it could significantly reduce the pores left by binder removal process in traditional method (i.e., gel-casting). Meanwhile, 0.9Al\(_2\)O\(_3\)–0.1TiO\(_2\) suspension with high solid loading and low viscosity coagulates rapidly, which is also beneficial to form dense and uniform microstructure. Therefore, the DCC-HVCI method will be an effective method to enhance performance of microwave dielectric ceramics in the future.

### 4 Conclusions

In this paper, the DCC-HVCI method has been successfully applied to prepare 0.9Al\(_2\)O\(_3\)–0.1TiO\(_2\) microwave dielectric ceramics. Suspension with high solid loading (50 vol\%) and low viscosity was prepared by adding 0.3 wt\% TAC and adjusting pH value to 10–12 at room temperature. 0.9Al\(_2\)O\(_3\)–0.1TiO\(_2\) green bodies with uniform microstructures were coagulated by releasing calcium ions from 8.0 g/L calcium iodate at 70 \(^\circ\text{C}\). After sintering at 1500 \(^\circ\text{C}\) for 4 h and annealing at 1100 \(^\circ\text{C}\) for 5 h, the Al\(_2\)TiO\(_5\) secondary phase was eliminated and the 0.9Al\(_2\)O\(_3\)–0.1TiO\(_2\) ceramics showed uniform microstructure with density of 3.62±0.02 g/cm\(^3\). The microwave dielectric properties of 0.9Al\(_2\)O\(_3\)–0.1TiO\(_2\) ceramics prepared by DCC-HVCI method were \( \varepsilon_r = 11.26\pm0.06, \ Q \times f = 11569\pm629 \ \text{GHz}, \ \tau_f = 0.93\pm0.60 \ \text{ppm/}^\circ\text{C}. \) The results suggested that the DCC-HVCI method would be a promising colloidal forming method to prepare complex-shaped microwave dielectric ceramics with good composition homogeneity and microwave dielectric properties in the future.

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