Study of $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 ceramics prepared by a novel DCC-HVCI method

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Abstract: In this paper, in-situ coagulation of $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 suspension and microwave dielectric properties of $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 ceramics prepared by a novel direct coagulation casting via high valence counter ions (DCC-HVCI) method were proposed. The $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 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 $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 suspension could be successfully prepared by adding 0.3 wt% TAC and adjusting pH value to 10–12 at room temperature. $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 green bodies with uniform microstructures were coagulated by adding 8.0 g/L calcium iodate after treating at 70 °C for 1 h. $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 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 $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 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; $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 ; DCC-HVCI

1 Introduction

With the rapid development of microwave communication technology, the demand of microwave dielectric ceramics with low dielectric constant (ε_r),

high quality factor ($Q\times f$), and near-zero temperature coefficient of resonator frequency (τ_f) is rising [1]. Al_2O_3 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 Al_2O_3 ceramics was limited by high τ_f (–60 ppm/°C) and sintering temperature (> 1600 °C) [5]. TiO_2 , on the contrary, has positive τ_f value, so a near-zero τ_f could be

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achieved by adding a certain amount of TiO_2 to Al_2O_3 [6]. Ohishi *et al.* [7] and Miyauchi *et al.* [8] found $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 ceramics had a near-zero τ_f , while a detrimental Al_2TiO_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_2TiO_5 secondary phase. Ohishi *et al.* [7] reported good dielectric properties of $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 ceramics with $\epsilon_r = 12.4$, $Q \times f = 117000$ 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 $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 ceramics with $\epsilon_r = 12.4$, $Q \times f = 148000$ GHz, $\tau_f = +1.5$ ppm/°C after annealing at 1100 °C.

At present, $0.9\text{Al}_2\text{O}_3$ – 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 $0.9\text{Al}_2\text{O}_3$ – 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 $0.9\text{Al}_2\text{O}_3$ – 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 [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 $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 microwave dielectric ceramics. Tri-ammonium citrate (TAC) was used as dispersant to prepare $0.9\text{Al}_2\text{O}_3$ – 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 $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 suspension. The influence of dispersant content, solid loading, and calcium iodate content on the rheological properties of the $0.9\text{Al}_2\text{O}_3$ – 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 $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 ceramics were investigated.

2 Experimental procedure

2.1 Raw materials

Commercial available Al_2O_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 $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 powders. The microstructures of Al_2O_3 and TiO_2 powders are shown in Figs. 1(a) and 1(b). The $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 powders were prepared by solid-state reaction method [13]. Figure 1(c) shows the microstructure of prepared $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 powders and Fig. 1(d) shows the EDS image of Ti distributing uniformly in $0.9\text{Al}_2\text{O}_3$ – 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 ($\text{Ca}(\text{IO}_3)_2 \cdot 6\text{H}_2\text{O}$) 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.

Fig. 1 Microstructures of (a) Al₂O₃ and (b) TiO₂ raw powders, (c) prepared 0.9Al₂O₃–0.1TiO₂ powders, and (d) EDS image of Ti in 0.9Al₂O₃–0.1TiO₂ powders.

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 (ϵ_r) and $Q \times f$ values were

Fig. 2 Flowchart of the experimental processes.

measured in the TE₀₁₁ 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 (τ_f) was calculated by the following formula:

$$\tau_f = \frac{1}{f(25)} \times \frac{f(75) - f(25)}{75 - 25} \quad (1)$$

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 0.9Al₂O₃–0.1TiO₂ 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% 0.9Al₂O₃–0.1TiO₂ suspension at different pH values. Without TAC, the isoelectric point of 0.9Al₂O₃–0.1TiO₂ 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 0.9Al₂O₃–0.1TiO₂ 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

Fig. 3 Zeta potential of 10 vol% 0.9Al₂O₃–0.1TiO₂ suspension at different pH.

absorption of citrate ions on the surface of 0.9Al₂O₃–0.1TiO₂ particles. The results above indicates that TAC improves the repulsive force between 0.9Al₂O₃–0.1TiO₂ particles, which is beneficial to the stable dispersion of the particles in the alkaline region. Therefore, the well-dispersed 0.9Al₂O₃–0.1TiO₂ 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% 0.9Al₂O₃–0.1TiO₂ suspension. The viscosities of 0.9Al₂O₃–0.1TiO₂ 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 0.9Al₂O₃–0.1TiO₂ 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 0.9Al₂O₃–0.1TiO₂ suspension increases. Hence, the proper dispersant content to prepare stable 0.9Al₂O₃–0.1TiO₂ 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

Fig. 4 Effect of TAC contents on the rheological properties of 25 vol% 0.9Al₂O₃–0.1TiO₂ suspension.

performance of final ceramic products. The relation between relative viscosity (η_r) and solid loading (ϕ) is commonly simulated by Dougherty–Krieger (D–K) model for monodispersed suspensions as following [32]:

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m} \quad (2)$$

where ϕ_m is the maximum packing fraction, and $[\eta]$ is the intrinsic viscosity. ϕ_m and $[\eta]$ are used to fit the experimental results and analyze the suspension structure. Figure 5 shows the relative viscosities of 0.9Al₂O₃–0.1TiO₂ suspensions with different solid loadings at a shear rate of 100 s^{−1}. The simulated relative viscosity can be expressed as

$$\eta_r = \left(1 - \frac{\phi}{0.702}\right)^{-7.101 \times 0.702} \quad (3)$$

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 0.9Al₂O₃–0.1TiO₂ suspension. Therefore, 0.9Al₂O₃–0.1TiO₂ suspension with solid loading of 50 vol% is selected.

3.2 Coagulation of 0.9Al₂O₃–0.1TiO₂ 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

Fig. 5 Relative viscosities of 0.9Al₂O₃–0.1TiO₂ suspensions with different solid loadings at a shear rate of 100 s^{−1}.

Ca²⁺ from calcium iodate with increasing temperature. The absorption of citrate ions (C₆H₅O₇^{3−}) from ionized TAC on the surface of 0.9Al₂O₃–0.1TiO₂ particles results in intense electrostatic repulsion and thus, stable dispersion of the suspension can be achieved. The dissolution reaction can be expressed as

Ca²⁺ has opposite charge to C₆H₅O₇^{3−} that could absorb on 0.9Al₂O₃–0.1TiO₂ particle surface, so the electrical double-layer is compressed and the electrostatic repulsion decreases, which causes the decrease of suspension stability. Furthermore, Ca²⁺ could react with C₆H₅O₇^{3−} and form calcium citrate, which is insoluble in water and promotes the precipitation of the suspension.

Figure 6 shows the effect of calcium iodate concentration on the viscosity of 50 vol% 0.9Al₂O₃–0.1TiO₂ 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

Fig. 6 Effect of calcium iodate concentration on the viscosity of 50 vol% 0.9Al₂O₃–0.1TiO₂ suspension at 25 °C.

Table 1 Coagulation time and state of green bodies prepared by DCC-HVCI method at different coagulation temperature

Coagulation temperature (°C)	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 °C and 40 °C), calcium iodate can hardly dissolve so that the content of high valence counter ions of Ca^{2+} 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 °C and 70 °C), the high valence counter ions of Ca^{2+} 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 °C, water in the $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 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 $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 suspension after treating at 70 °C presents a homogeneous composition without cracking and possesses the relatively short coagulation time of 60 min. Therefore, the coagulation temperature of 70 °C is chosen for the direct coagulation casting.

3.3 Properties of green bodies and $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 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 $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 ceramics.

Fig. 7 (a) Photograph and (b) microstructure of green bodies prepared by DCC-HVCI method with 0.3 wt% TAC and 8.0 g/L calcium iodate.

Figure 8 shows the XRD patterns of different $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 ceramic samples. There are Al_2O_3 , TiO_2 , and Al_2TiO_5 phases in $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 ceramics after sintering at 1500 °C for 4 h (see Fig. 8(b)). Ohishi *et al.* [7] announced that Al_2TiO_5 tends to decompose to Al_2O_3 and TiO_2 in the temperature range of 1000–1200 °C due to its low thermal stability. As shown in Fig. 8(a), after annealing treatment, there are only Al_2O_3 and TiO_2 phases existing in the ceramics, while the peak intensities of Al_2O_3 and TiO_2 phases increase due to the decomposition of Al_2TiO_5 . The XRD patterns show that the annealing treatment has successfully eliminated the Al_2TiO_5 secondary phase, which ensures good microwave dielectric properties of $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 ceramics. Figure 9 shows the microstructure of $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 ceramics sintered at 1500 °C for 4 h and annealed at 1100 °C for 5 h. No obvious pores and uniform microstructures have been observed in the $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 ceramics prepared by DCC-HVCI method, which is beneficial for improving properties of the ceramics.

The density of the $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 ceramics prepared by DCC-HVCI method is $3.62 \pm 0.02 \text{ g/cm}^3$ and the microwave dielectric properties of $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2

Fig. 8 XRD patterns of different samples: (a) $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 ceramics after annealing at 1100 °C for 5 h, (b) $0.9\text{Al}_2\text{O}_3$ – 0.1TiO_2 ceramics after sintering at 1500 °C for 4 h.

Fig. 9 Microstructure of 0.9Al₂O₃–0.1TiO₂ ceramics sintered at 1500 °C for 4 h and annealed at 1100 °C for 5 h.

ceramics prepared by DCC-HVCI method are $\varepsilon_r = 11.26 \pm 0.06$, $Q \times f = 11569 \pm 629$ GHz, $\tau_f = 0.93 \pm 0.60$ ppm/°C. The good properties of 0.9Al₂O₃–0.1TiO₂ microwave dielectric ceramics are obtained due to the elimination of the Al₂TiO₅ 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, 0.9Al₂O₃–0.1TiO₂ 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 0.9Al₂O₃–0.1TiO₂ 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. 0.9Al₂O₃–0.1TiO₂ green bodies with uniform microstructures were coagulated by releasing calcium ions from 8.0 g/L calcium iodate at 70 °C. After sintering at 1500 °C for 4 h and annealing at 1100 °C for 5 h, the Al₂TiO₅ secondary phase was eliminated and the 0.9Al₂O₃–0.1TiO₂ ceramics showed uniform microstructure 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 $\varepsilon_r = 11.26 \pm 0.06$, $Q \times f = 11569 \pm 629$ GHz, $\tau_f = 0.93 \pm 0.60$ ppm/°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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