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The fabrication and characterisation of low-*k* cordierite-based glass–ceramics by aqueous tape casting

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Abstract

In this work, cordierite-based glass ceramic tapes were prepared by tape casting from suspensions containing different solids loading and different average particle sizes (PS). Three different empirical models were used to fit the experimental data from relative viscosity measured at a fixed shear rate (500 s^{-1}) versus solids loading. The green tapes were characterised by using scanning electron microscopy (SEM) and Hg porosimetry. The results showed that high values of solids volume fraction and PS ratio between glass and cordierite powders favour homogeneous and dense substrates. The dielectric properties of the sintered tapes were also measured, which met the requirements for the substrates in microelectronic and packaging industries.

Keywords: Cordierite; Dispersant; Glass ceramics; Rheological behaviour; Tape casting

1. Introduction

Cordierite is a promising low-*k* material in microelectronic and packaging industries due to its low dielectric constant and low dielectric loss.[1,2] Its potential application requires the fabrication of high-quality substrates by tape casting,[3] which is a common technology for the fabrication of electroceramics as substrates for multilayer capacitors (MLC) and for multichip modules (MCM).

The slurries for tape casting usually involve non-aqueous- or aqueous-based systems.[4] Non-aqueous systems exhibit faster drying rates and enable to obtain thicker tapes. Meanwhile, it has already been established at an industrial scale. Contrarily, the development stage of aqueous tape casting processes is still at lab scale. Because of economical and environmental-friendly, aqueous-based system is considered as an alternative for non-aqueous tape casting, which has been successfully used to prepare crack-free high-quality tapes through carefully controlling the process parameters, such as type and amount of dispersant and binder, solid loading and so on.[5]

It is well known that solids loading and PS of the powders are both critical factors affecting rheological behaviour of the slurry and in turn, the microstructure and properties of the green and sintered bodies consolidated by colloidal shaping techniques.[6–9] Zupancic et al.[6] investigated the influence of solids loading on rheological properties of aqueous α-Al_2O_3 suspensions and found that the flow behaviour changed with increasing solids loading. Furthermore, the apparent yield stress was a significant quantity for characterising changes in structural conditions of the disperse phase. Bergström[7] compared the volume fraction dependence of the high shear viscosity of three different silicon nitride powders. All of them could be fitted to a modified Krieger–Dougherty model, whereas the Quemada or the Krieger–Dougherty equations did not give a satisfactory fit. Based on the steady shear measurements, it was deduced that the difference was related to effective volume effects and the physical characteristics of the powders. Similar results were also observed for silicon carbide slurries,[9] in which a predominant electrostatic stabilisation mechanism determined the electrostatic nature and the longer range of the inter-particle forces in the suspensions, and therefore, a thicker adlayer of about 20–22 nm, compared with 8–12 nm estimated for the sterically stabilised silicon nitride suspensions.[7] Furthermore, solids loading affected the properties of the green bodies. In some systems, green densities could initially show an increase to a maximum, followed by a decreasing trend with increasing solids loading.[9–11] A linear increase in packing density with solid loading was

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also observed in some other suspensions.[12,13] However, no relationship between solids loading and green density was found in other systems.[14,15]

Compared with the effect of solids loading in the process of tape casting, the effect of particle size (PS) of the powder is extremely complicated. For single component systems, its effect is relatively simple. However, it became much more difficult to be evaluated for the multiple-components system.[16] Monosize sphere powder was considered as an ideal model in colloidal system, in which the maximum solids loading of about 74 vol.% in an octahedral or tetrahedral arrangement could be theoretically achieved. However, this monosized sphere arrangements have domains inside the green bodies, leading to large pores, flaws and cracks.[17] On the other hand, the use of bimodal powder can prevent broad pore size distribution and obtain relative high green density.[9] Zheng et al.[18] studied the packing density of binary powder mixtures and developed an empirical equation, describing the relationship between the packing density and initial packing efficiencies of particles, the particle size ratio and the volume fraction variations of the system. The packing density was lower when the size ratio of coarse particle to fine particles decreased.

Generally, the solids loading should be as high as possible to decrease drying time and in turn, to decrease the shrinkage in the process of binder removal and sintering. Therefore, the aim of this work is to obtain high solids loading suspension for aqueous tape casting, leading to homogeneous and dense microstructure. So far, for the cordierite–glass system, there are few reports about the fabrication of green tapes by aqueous tape casting. The optimisation of some parameters in the process has been performed in previous work.[3] The emphasis of this work will be given to the investigation of the effect of solids loading and average PS of glass particles on the rheological behaviour of the slurry and in turn, on the microstructure and property of the green and sintered body.

2. Experimental procedures

The cordierite powder used in the present work was synthesised at the lab (D_{50} = 0.8 μm).[11] A glass powder (Schott glass package, Germany) with an average PS (D_{50} = 4.2 μm), was used as starting raw material, either as received or after milling up to two different mean particle sized powders (D_{50} = 2.8 μm and 1.8 μm, respectively). Suspensions with different starting solids contents (ranging from 60 to 85 wt.%) and different glass powders (D_{50} = 4.2, 2.8 and 1.8 μm) were prepared by mechanically mixing cordierite and glass powders in a weight ratio of 50:50 into distilled water with 1.0 wt.% (relative to the solid content) of Dolapix CE 64 (Zschimmer & Schwarz, Germany) as dispersant. After being stirred for 30 min for uniform distribution of the components, the obtained slurries were deagglomerated in polyethylene bottles using ZrO_2 balls for 6 h. The binder (Duramax B-1080, Rohm and Haas, USA) was then added to the as-prepared suspension. Subsequently, a de-airing and conditioning step was performed for further 6 h by rolling the slips in the milling container without balls. The green tapes were prepared by casting the as-prepared suspensions onto a plastic film [Polypropylene (PP), Western Wallis, USA] with a laboratory tape caster (Elmetherm, Oradour Sur Vayres, France) at room temperature (≈20 °C) and humidity (≈40% RH). A gap of 300 μm under the blade and a fixed casting speed of (≈6 mm/s) were selected for tape casting.

Rheological properties of the suspensions were determined with a rotational control stress rheometer (Carri-med 500 CSL, UK). The measurements were performed at a constant temperature (20 °C). The adopted measuring configuration was a cone and plate, and steady measurements were conducted at shear rates from about 0.01 to 1000 s^{-1}. A pre-shearing was performed at the higher shear rate for 1 min before measurement, followed by an equilibrium time for 30 s to transmit the same rheological history to the whole tested suspensions. Pore-size distribution was examined by Hg-intrusion porosimetry (Poresizer 9320, Micromeritics, USA). The microstructural evolution of green bodies and sintered bodies was observed using scanning electron microscopy (SEM; 4100-1, Hitachi, Japan).

Before measurements of dielectric properties, an electro-depositor (Polaron Equipment Limited, SEM Coating Unit E5000) was used to deposit gold electrodes on both sides of sintered tapes, which derived from the suspension containing 80 wt.% solids when D_{50} for glass and cordierite particles was set at 4.2 and 0.8 μm, respectively. A Keithley 3330 LCZ Meter (Keithley, USA) was used to measure capacitance and loss factor of the tapes. The capacitance and the loss factor measurements were carried out at different frequencies (10^2–10^6 Hz), at room temperature. Dielectric permittivity was determined from the measured capacitance value.[19]

3. Results and discussion

3.1. Effects of PS and solids loading of glass powders on rheology of suspensions

The influence of the mean PS of the glass powders on rheological behaviour of the suspension was first studied using suspensions containing a total solids loading of 60 wt.%. Fig. 1 shows that the stress values required for flowing along all the shear rate range and the shapes of flow curves strongly depend on the mean PS of the

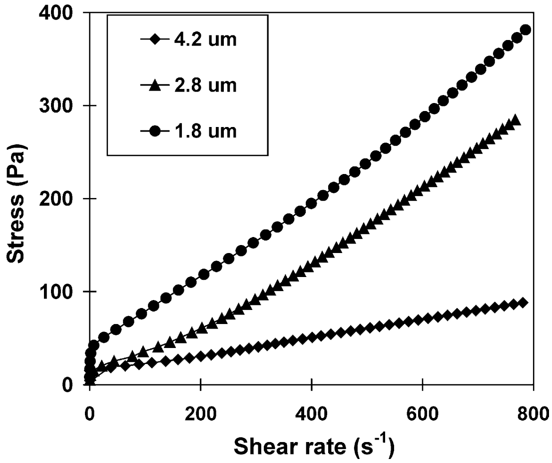

Fig. 1. Shear tress versus shear rate for suspension containing a total solids loading of 60 wt.% with different mean PS of glass powders (cordierite: $D_{50}=0.8$ μm).

glass component. The suspension with coarser glass powder displays a near Bingham plastic behaviour with a relatively small apparent yield stress value ($\tau_y \leqslant 20$ Pa). As the mean PS of the glass component decreases, the apparent yield stress becomes more accentuated with $\tau_y \approx 50$ Pa for the finest glass powder. Further, at moderate shear rates, the shear stress values required for flowing increase more than predicted by the Bingham model indicating a shear-thickening trend. This means that the systems become more interactive from the hydrodynamic point of view as the size of glass particles decreases. Two complementary reasons account for the observed evolution of the flow properties with the mean PS of glass component: (1) since the suspensions do not behave as hard sphere systems, the collisions between particles are mediated by the adlayer, the thickness of which is assumed to be approximately constant under similar dispersion conditions (pH of the suspending medium and amount of dispersant). This means that the ‘‘interaction size’’ of the dispersed particles is larger than the actual size, i.e. the ‘‘hard size’’ and their effective volume will increase as the specific surface area of the powder increases; (2) on the other hand, the packing ability of the particles in suspension decreases with decreasing the size ratio between the mean PS of the two powder components, cordierite and glass. The dispersing liquid phase will be more and more compromised in filling the interstitial spaces among particles, becoming less available for flowing.

Because of the earlier mentioned reasons and in order to enhance the solids loading in the suspension in an attempt to reduce drying shrinkage and the trend for cracking appearance and in turn, to increase the critical cracking thickness of the tapes, the coarser glass powder was selected for further investigating the effects of solids loading on rheology.

Fig. 2 shows the relative viscosity values measured at 500 s^{-1} versus solids loading of the suspensions. The ability of several models to fit the experimental data was tested, namely, the modified Krieger–Dougherty model (Eq. 1),[7] the Krieger–Dougherty model[20] (Eq. 2) and the Quemada model[21] [Eq. (3)]. The last two models have been proposed to describe the dependence of viscosity on solids loading of hard-sphere suspensions.

$$\eta_r = \frac{\eta}{\eta_0} = \left(1 - \frac{\phi}{\phi_m}\right)^{-n} \tag{1}$$

$$\eta_r = \frac{\eta}{\eta_0} = \left[1 - \frac{\phi}{\phi_m}\right]^{-[\eta]\phi_m} \tag{2}$$

$$\eta_r = \frac{\eta}{\eta_0} = \left(1 - \frac{\phi}{\phi_m}\right)^{-2} \tag{3}$$

where η_r, η, and η_0 is the relative viscosity, viscosity of the suspension and that of the liquid medium, respectively. The intrinsic viscosity, $[\eta]$, relates to the effect on the relative viscosity of non-interacting particles in very dilute suspensions. $[\eta]$ is 2.5 for spheres and is expected to increase with increasing anisotropy of the dispersed particles. ϕ_m is the maximum volume fraction and n is a constant.

It can be observed that a good fitting of the experimental data to the modified Krieger–Dougherty model could be obtained, yielding $\phi_m \approx 70$ vol.% and $n=2.7$ (Fig. 2). The other two models could not give a good fitting. This suggests that the system does not behave as a hard-sphere model, whose exponent n should be 2.5 (the Einstein coefficient for spheres). This coefficient would increase as the particles' shape deviates from the

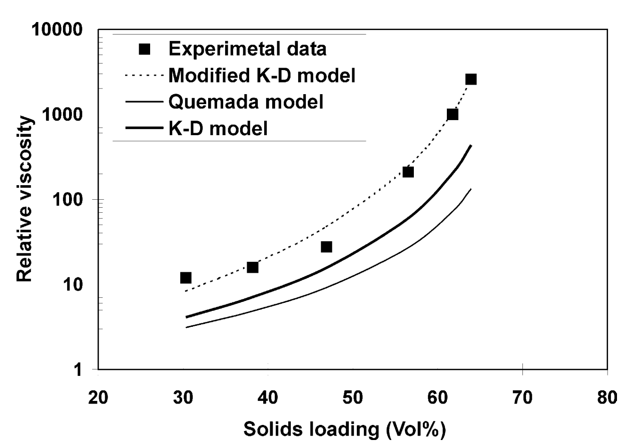

Fig. 2. Relative viscosity of the suspensions measured at 500 s^{-1} versus solids volume fraction.

spherical one, which reflects the slightly anisotropic characteristics of the particles as observed by SEM.[19]

These results are according to the predictions made concerning the distinction between the "hard size" and the "interaction size", confirming that collisions between particles are mediated by the adlayer that increases the apparent size of the dispersed particles and thus, their effective volume.

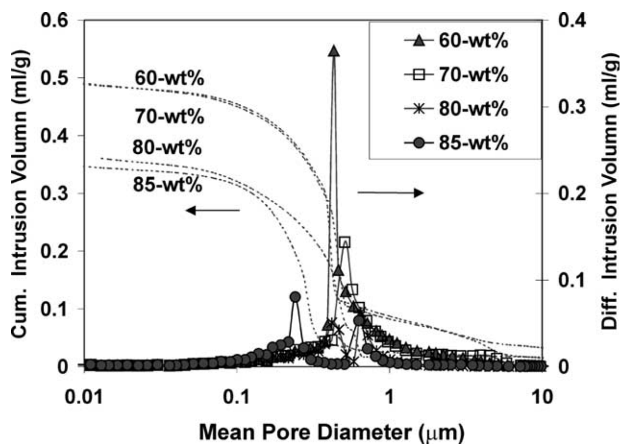

Fig. 3. Pore size distributions of the samples derived from suspensions containing different solids loading.

3.2. *Effect of solids loading and PS ratio on the properties of green and sintered tapes*

Fig. 3 shows pore size distributions of the samples derived from suspensions containing different solids loading with the coarse glass powders ($D_{50}=4.2$ μm). The sample containing 60 wt.% solids exhibits the highest porosity. The porosity gradually decreases with increasing solids loading. The difference between porosities of the samples derived from suspensions containing 60 wt.% (40.5%) and 70 wt.% (37.2%) solids is small. As solids loading increased to 80 wt.%, the influence of solids loading on the porosity became more significant, in which the porosity was about 33.5%. Finally, the porosity decreased to about 31.3% when the solids loading reached about 85 wt.%, having a highest green density (1.75 g/cm^3). The obtained green densities varied in the range of 59.5–68.7% TD, which are higher than those measured for Al_2O_3 green tapes (50–56.28% TD).[22]

The microstructural evolution of the green tapes with increasing solids loading as observed by SEM is shown in Fig. 4. The tape derived from the slurry containing 60 wt.% solids has a heterogeneous microstructure with large pores, in which tiny cordierite particles do not completely occupy all the voids between irregular and

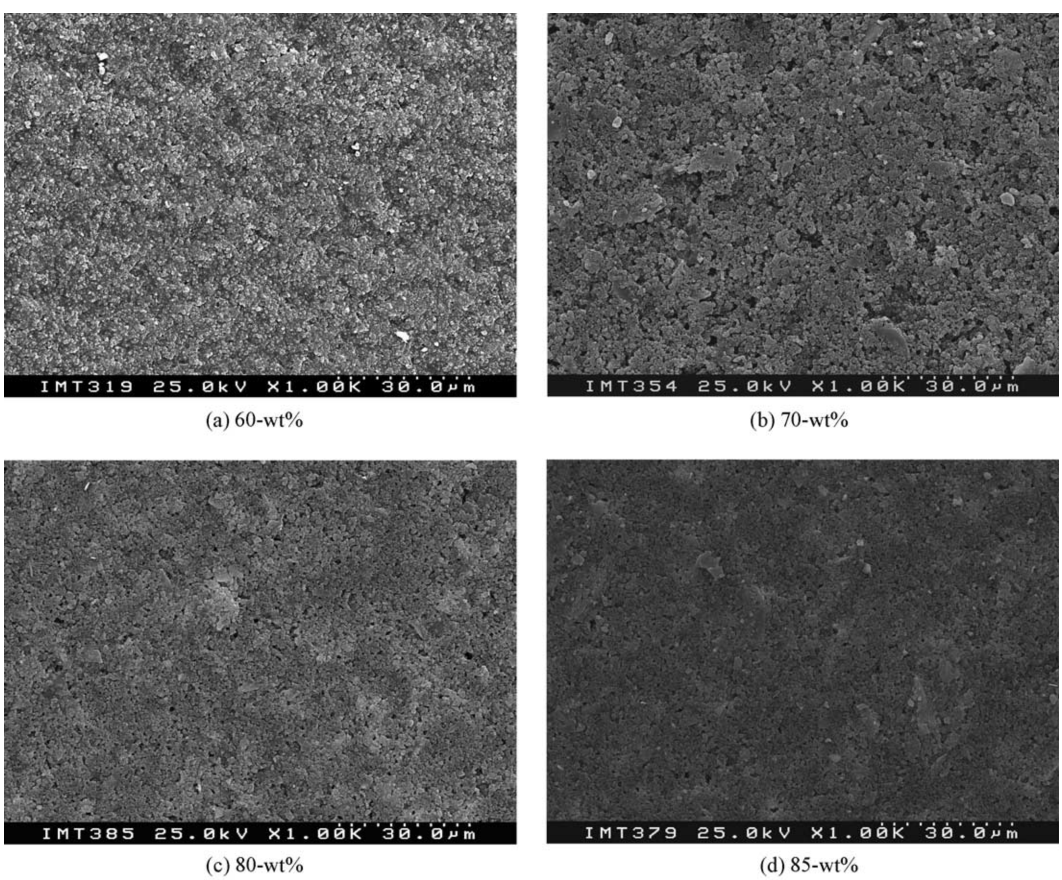

Fig. 4. Microstructural evolution of the green tapes derived from suspensions with different solids loading: (a) 60 wt.%; (b) 70 wt.%; (c) 80 wt.%; (d) 85 wt.%.

coarse glass particles. As solids loading gradually increasing from 70 to 85 wt.%, the microstructure of the green tapes became more homogeneous and denser. These observations coincide with the porosity measurements very well.

Fig. 5 displays the pore size distributions of the green tapes obtained from the suspensions containing 60 wt.% solids and 10 wt.% binder with different PS of glass powders. The green tape with the coarse glass powder exhibits a broader pore size distribution, including a higher amount of large pores. A narrowing trend of pore size distribution is observed as PS of glass powder decreases; the representative peaks become more intense, denoting also an increase in total porosity. In fact, the porosity value is about 40.5, 45.3 and 46.5% for the tapes containing coarse, intermediate and fine glass powder, respectively. The increase in porosity can be attributed to insufficient occupation of the tiny cordierite particles into the voids created among the coarser glass particles when the ratio between the average particle sizes of glass and cordierite decreases (about 2.3 for fine glass powder), compared with the other two samples (3.5 for the intermediate powder, and about 5.2 for the coarser one). These results support the interpretation about the effect of mean PS of glass component on flow properties of the suspensions (Fig. 2). They are also in good agreement with the observations performed by Zheng and his co-workers,[18] in which the packing density is lower when the PS ratio between coarse and fine particles decreased.

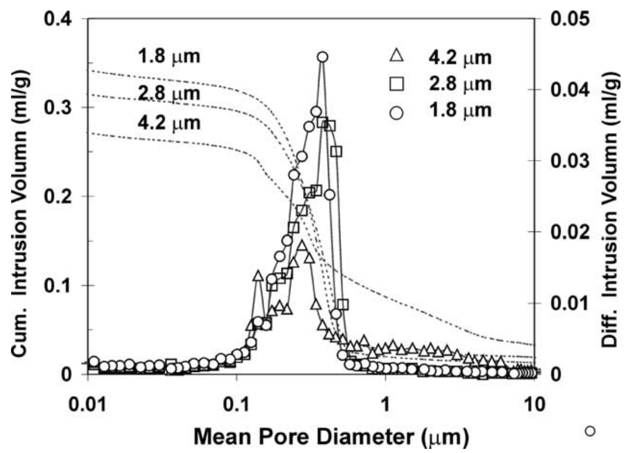

Fig. 5. Pore size distribution of the green tapes with different PS of glass powders.

The microstructures of the above tapes heat-treated at 1150 °C for 2 h are shown in Fig. 6. It can be observed that the sintered tapes became gradually denser with increasing

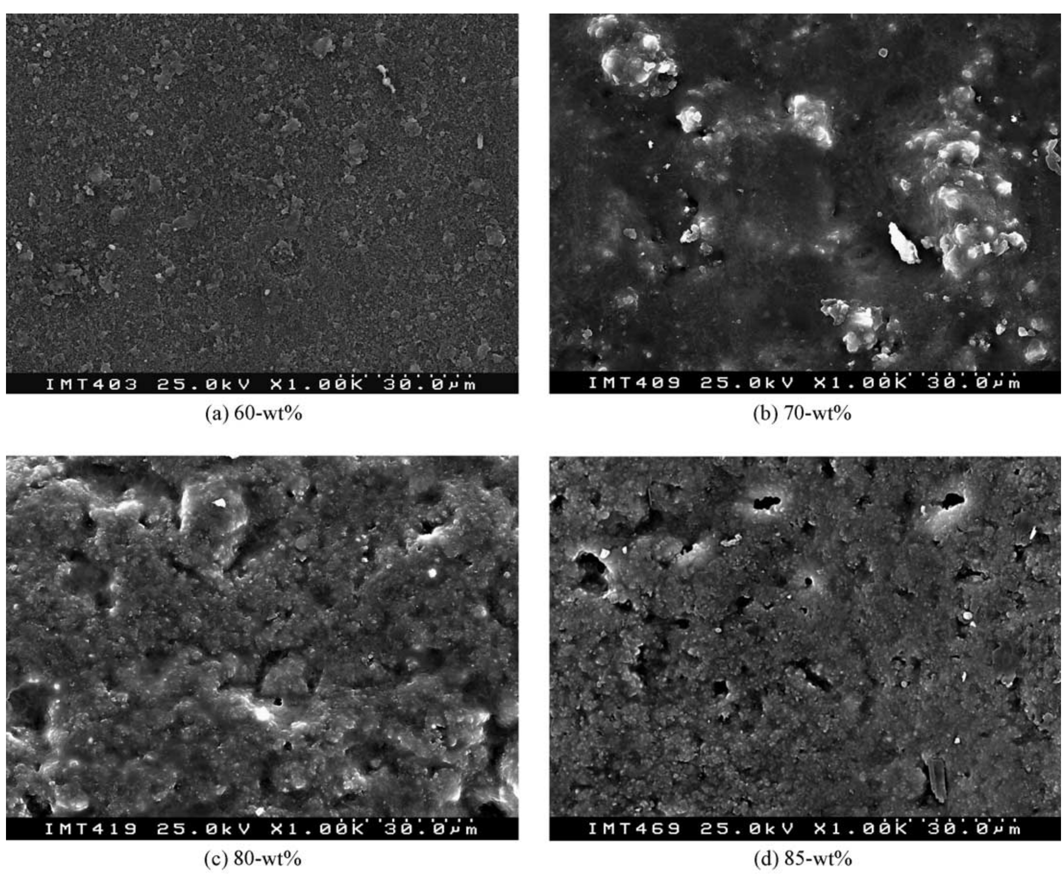

Fig. 6. Microstructures of the tapes prepared from suspensions with different solids loading after sintering at 1150 °C for 2 h: (a) 60 wt.%; (b) 70 wt.%; (c) 80 wt.%; (d) 85 wt.%.

solids loading. The dielectric constant and the dissipation factor of the sintered tape (85 wt.%) at 1150 °C/2 h was about 5 and 0.01 at 1 MHz, respectively. Both values are comparable with those reported elsewhere.[23,24]

4. Conclusions

In this work, cordierite–glass green tapes were successfully fabricated via aqueous tape casting. The viscosity of the suspensions increased with solids content, whereas the apparent yield stress (τ_y), as well as the shear stress values required for making the systems to flow with increasing shear rates became more pronounced with decreasing the mean PS of the glass powder component. The calculated maximum solids loading (ϕ_m) of the suspension was ≈70 vol.% when the mean PS of glass and cordierite were about 4.2 and 0.8 μm, respectively. Meanwhile, homogeneous and dense substrates could be achieved when the solids content was about 85 wt.% and PS ratio between glass and cordierite powders was about 5.2. The dielectric constant of the sintered bodies at 1150 °C/2 h was around 5 and the dissipation factor was about 0.01 at 1 MHz.

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