

# Sintering, crystallization and properties of MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system glass-ceramics containing ZnO

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## Abstract

The effect of replacement of Al<sub>2</sub>O<sub>3</sub> by ZnO on the sintering and crystallization behavior of MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system glass-ceramics was investigated. The results show that with increasing ZnO content, the melting temperature and crystallization temperature of the glass-ceramics were lowered, and the glass transition temperature firstly decreased and then increased. With the replacement of 5 and 8 wt.%, the predominant crystalline phase in the glass-ceramics was found to be  $\alpha$ -cordierite and the secondary crystalline phase to be gahnite and quartz. When the replacement was increased to 11 wt.%, the predominant crystalline phase was found to be gahnite and quartz and the secondary phase to be  $\alpha$ -cordierite. Only the sample containing 8 wt.% ZnO (abbreviated as sample Z8) can be fully sintered before 1000 °C. Therefore, a dense and low dielectric loss glass-ceramic with predominant crystal phase of  $\alpha$ -cordierite and gahnite is achieved by using fine glass powders ( $D_{50} = 3 \mu\text{m}$ ) fired at 900–925 °C. The as-sintered density approaches 97.0% theoretical density. The flexural strength of sample Z8 increases with sintering temperature, which closely corresponds to its relative density. The thermal expansion coefficient (TCE) of sample Z8 sintered at different temperatures mainly depends on its crystalline phases. The dielectric property of sample Z8 sintered at different temperatures depends on not only its relative density but also its crystalline phases. The dense and crystallized glass-ceramic Z8 exhibits a fairly low dielectric constant (5.0–5.2), a low dielectric loss ( $\leq 10^{-3}$ ) at 1 MHz, a low thermal expansion coefficient ( $4.0\text{--}4.2 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ), very close to that of Si ( $\sim 3.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ) and a higher flexural strength  $\geq 125 \text{ MPa}$ , suggesting that it would be a promising material in the electronic packaging field.

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**Keywords:** Glass; X-ray diffraction; SEM; Thermal expansion; Dielectric property

## 1. Introduction

Due to the high frequency transportation for wide applications in the wireless communications and computer fields, low dielectric constant, low temperature co-fired ceramics (LTCC) package have been developed to achieve the requirements of high signal propagation speed, good reliability and low cost [1–3]. “Low temperature” means that ceramic substrates should be sintered at less than 1000 °C in order to be co-fired with copper (1083 °C), silver (961 °C) or gold (1061 °C). Several material systems such as glass plus ceramics [4,5] and glass-ceramics have been developed to meet the requirements in applications

for LTCC. Glass-ceramics formed by controlled crystallization of glass are materials of high crystalline grade. Properties such as lower dielectric constant, appropriate thermal expansion coefficient (TCE) and cofirability with other materials, make glass-ceramic compatible with the high performance multilayer ceramic substrates [6–7].

Cordierite (2MgO·2Al<sub>2</sub>O<sub>3</sub>·5SiO<sub>2</sub>) based glass-ceramics are attractive materials for preparing low firing temperature substrates due to their low dielectric constant and matching thermal expansion coefficient of single crystal silicon [1,6–7]. However, cordierite glass has a high melting temperature ( $\geq 1600 \text{ }^\circ\text{C}$ ). It is difficult to obtain dense glass-ceramics below 1000 °C because the cordierite-based glasses have high viscosity and narrow sintering temperature range [3]. Because glass powder sintering proceeds by viscous flow [8], the decreasing glass viscosity shows good effect on its sinterability. In order to fabricate dense glass-ceramics, it may be a critical factor to

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Table 1  
Composition of the glass samples (wt.%)

Sample	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	ZnO	Sb <sub>2</sub> O <sub>3</sub>
Z0	13.7	34.7	51.6	1.5	0	0.5
Z5	13.7	29.7	51.6	1.5	5	0.5
Z8	13.7	26.7	51.6	1.5	8	0.5
Z11	13.7	23.7	51.6	1.5	11	0.5

select adequate glass composition and flux, which reduces glass viscosity.

Several studies have been conducted on the nucleation and crystallization of cordierite glass-ceramics [9–11], and some are related to the low temperature sintering behavior of cordierite-based glass-ceramics [12–13]. It was found that an addition of ZnO in lithium aluminosilicate (LAS) glass-ceramics can lower the melting point and glass transition temperature and improve the thermal expansion coefficient of glass-ceramics [14–16]. According to our knowledge, there has been no report on low temperature preparation of glass-ceramics with the stoichiometric cordierite composition doped with ZnO.

The aim of the present study was to investigate the effect of replacement of Al<sub>2</sub>O<sub>3</sub> by ZnO on the sintering and crystallization behavior of MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system glass-ceramics. The physical properties such as dielectric properties and thermal expansion characteristics were also evaluated.

## 2. Experimental

The starting materials were analytical grade: SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, H<sub>3</sub>BO<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub> and ZnO. The detailed proportions of the glasses are given in Table 1. Sb<sub>2</sub>O<sub>3</sub> was added due to its promising clarifying effect. A glass batch of homogeneous mixture was prepared by ball milling and then melted in alumina crucibles at 1540–1560 °C for 4 h in an electric furnace and then quenched in distilled water to form frits, which were crushed and wet-milled for 50 h. The mean particle sizes of the glass powders were measured with a particle size analyzer to be about 3 μm. Non-isothermal reaction analysis of the glass powders was investigated using a thermoanalyzer with a heating rate of 10 K/min in air.

To prepare the bulk samples, the obtained glass powders were granulated with 3% poly (vinyl alcohol) (PVA) and then were pressed into disks and rectangle strips under a uniaxial pressure of 100 MPa. Glass-ceramics were obtained by isothermal heat treatment of the samples at temperatures higher than 800 °C in air. Phase evolution in the samples was identified by X-ray powder diffraction (XRD, D8-Advance, Bruker) using Cu Kα radiation. Density of the bulk glass-ceramic samples was measured by the Archimedeian method using distilled water as medium. Dielectric properties were measured by a LCR meter (HP4284A, Agilent) at 1 MHz and at room temperature. Average linear thermal expansion coefficient from room temperature to 300 °C was measured in air at a heating rate of 10 K/min using a dilatometer (DIL 402C, NETZSCH). The flexural strength was measured using a 3-point bending strength with a span of 30 mm at a crosshead speed of 0.5 mm/min. The morphologies of crystalline phases developed on heat treatment of the glass samples were examined by scanning electron microscopy (SEM, JSM-5610LV). The polished samples were given a light etched with 2.5 M HF for 30 s.

## 3. Results and discussion

### 3.1. Crystallization behavior

Fig. 1 shows the DTA traces of glasses under a non-isothermal heat treatment at a constant heating rate of 10 K/min. From

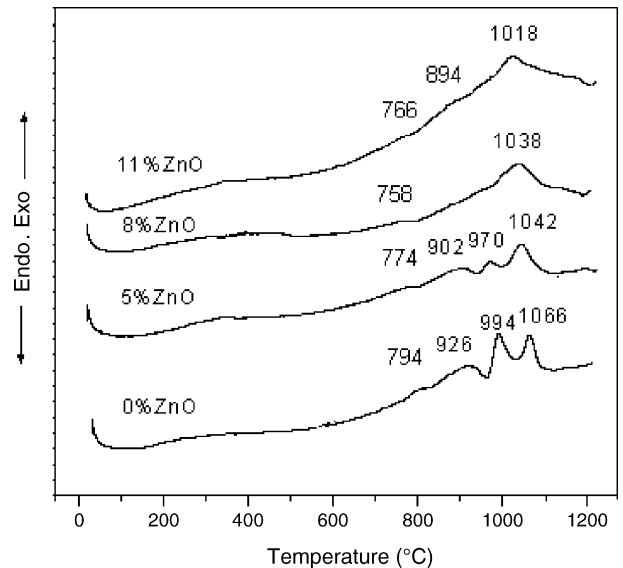
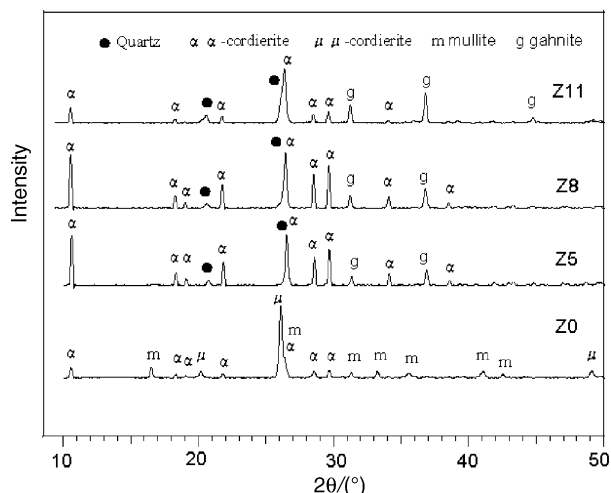


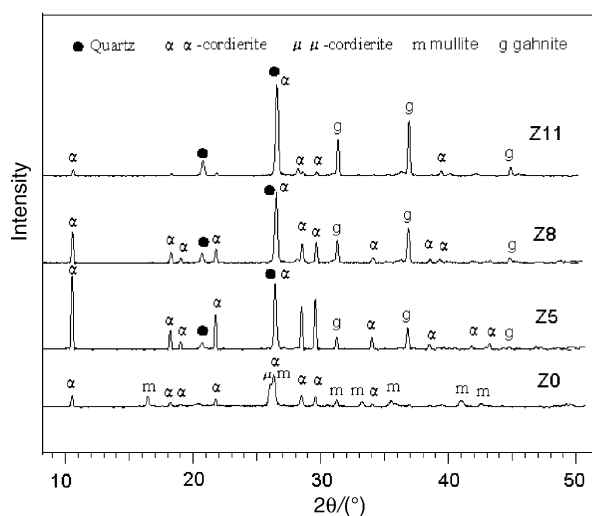
Fig. 1. DTA traces of the glass powders at a heating rate of 10 K/min.

Fig. 1, it is observed that samples Z0 and Z5 exhibit three exothermic peaks. Sample Z8 exhibits only one exothermic peak ( $T_p$ ). With increasing ZnO content from 0 to 8 wt.%, both glass transition temperature ( $T_g$ ) and crystallization peak temperature ( $T_p$ ) of glass samples decrease as shown in Fig. 1. The glass transition temperature ( $T_g$ ) and the crystallization temperature ( $T_p$ ) decrease can be attributed mainly to the decrease of the melt viscosity with increasing ZnO content. It is clear that the crystallization peak gets to broaden with an increase content of ZnO. As increasing ZnO content to 11 wt.%, the glass transition temperature ( $T_g$ ) also elevates to 766 °C, and sample Z11 here represents two exothermic peaks in the DTA trace. The exothermic peak at 894 °C is weak, and another peak (at 1018 °C) height and sharpness increase. The above results indicate that the replacement of Al<sub>2</sub>O<sub>3</sub> by ZnO influences the crystallization process of the glasses. It was believed that a small quantity of ZnO substituting for Al<sub>2</sub>O<sub>3</sub> can reduce transition temperature of the glass, retard the crystallization of the glass, increase a range between  $T_g$  and  $T_p$  and improve the sintering densification of glass-ceramics. Whereas, overfull ZnO (11 wt.%) will accelerate the crystallization of glasses and then increase the glass viscosity and finally restrain the sintering densification of glass-ceramics. The reason may be that zinc divalent ion ( $Zn^{2+}$ ) has a higher intensity of electric field, leads to phase separation in the glass and reduces the crystallization activation energy of the glass [16].

Fig. 2 shows the XRD patterns of each glass powders after heat treatment. From Fig. 2a, it was found that the predominant crystalline phase in sample Z0 was  $\mu$ -cordierite and the minor crystalline phases were  $\alpha$ -cordierite and mullite. In sample Z5, the main phase was  $\alpha$ -cordierite, some amount of gahnite and a trace of quartz appeared. In sample Z8,  $\alpha$ -cordierite as the main phase, gahnite and quartz all increased. In sample Z11, the main phase had become gahnite,  $\alpha$ -cordierite obviously decreased and quartz slightly increased. When the glass powders were heated at 1000 °C for 2 h as shown in Fig. 2b, the main phase was  $\alpha$ -cordierite and mullite, and  $\mu$ -cordierite still existed in sample



(a) Heated at 900 °C for 2 h.



(b) Heated at 1000 °C for 2 h.

Fig. 2. (a and b) XRD patterns of the samples after heat treatment.

Z0. With increasing ZnO content substituting for  $\text{Al}_2\text{O}_3$  (from 5 to 11 wt.%), both gahnite and quartz evidently increased, and  $\alpha$ -cordierite clearly decreased. In sample Z11, gahnite and quartz determinately became the main crystalline phases. The precipitation of quartz in samples may be attributed to the formation of gahnite phase, which resulted in an increase of  $\text{SiO}_2$  content in the residual glass phases and be in favor of the precipitation of quartz in the glasses [17–19].

### 3.2. Sintering behavior

The relative density for the fired samples in the temperature range between 800 and 1000 °C is illustrated in Fig. 3. The relative density equals the theoretical density of a sample divided by its apparent density. The relative density for the samples increased as the ZnO content increased. Although high densification rate in all samples took place between 850 and 900 °C, it is interesting that only sample Z8 has better sintering behavior. At 900 °C, the relative density of sample Z8 has reached 97%, which indicates that sample Z8 gets to almost full densification.

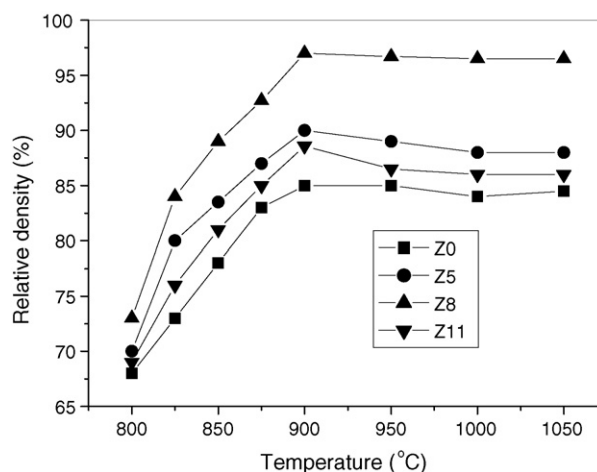


Fig. 3. Relative densities of the samples heated at various temperatures.

Such a high rate of densification for sample Z8 is thought to be attributed to the lowest glass transition temperature (as seen in Fig. 1) and the viscous glass phase during the firing process [7–8,13]. When sintering temperature exceeds 900 °C, the relative density of sample Z8 slightly decrease, which is thought to be quartz precipitated markedly [5].

The optimum heat treatment procedures for a dense and crystallized glass-ceramic could be developed by considering the following factors. (1) Transition temperature of glass,  $T_g$ : it determines the starting sintering temperature. In forming useful LTCC substrates, it is important that no sintering occurs before the complete binder burnout [20]. The binder decomposition temperature is usually in the range of 400–700 °C. (2) Crystallization temperature ( $T_p$ ): it determines the temperature that the crystal phase starts to grow. When crystallization occurs, it would decrease the densification. Usually the crystallization temperature must be below 950 °C for LTCC application. (3) Sintering rate: whether glass-ceramic powders can be fully sintered before densification stops depends on the sintering rate. It is revealed that both factors (1) and (2) contributes the temperature region for efficient densification.

In present study, sample Z8 has been evaluated in an efficient densification range from 800 to 900 °C. This meets the requirements of factors discussed above and is suitable for using in LTCC substrates fabrication. Full densification specimens can be achieved before the occurrence of crystallization at 1038 °C in this work using micron-scale glass powders. A completely sintered sample Z8 with  $\alpha$ -cordierite and gahnite phases is obtained between 900 and 1000 °C. Fig. 4 shows the SEM of polished surfaces of sample Z8 sintered at different temperatures. Sample Z8 sintered at 1000 °C has more pores than at 900 °C. This indicates that the degree of densification in sample Z8 sintered at 900 °C is higher than that in the one sintered at 1000 °C, which corresponds to the relative density of sample Z8 as shown in Fig. 3.

### 3.3. Physical properties

Except for sample Z8, all of samples Z0, Z5 and Z11 are incapable of full densification before 1000 °C. It is essential that the

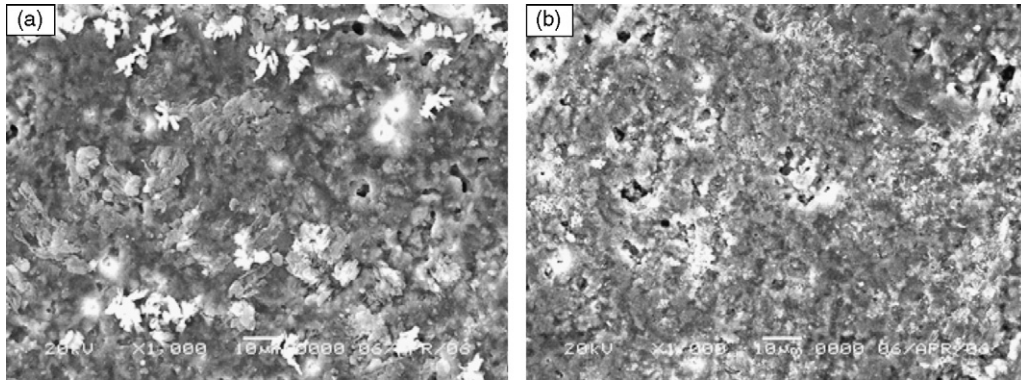


Fig. 4. SEM photographs of the etched sample Z8 sintered at different temperatures for 2 h: (a) 900 °C; (b) 1000 °C.

characteristics of sample Z8 were understood in detail. Fig. 5 shows X-ray diffraction results of sample Z8 sintered at different temperatures. It showed the progressive phase changes of the glass from amorphous to the crystalline state with increasing heat-treat temperature. When heated at 800 °C,  $\mu$ -cordierite appeared. At 850 °C, the main phase is still  $\mu$ -cordierite and a small amount of  $\alpha$ -cordierite occurred. As the heat treatment temperature was raised to 900 °C,  $\alpha$ -cordierite as the predominate phase appeared and  $\mu$ -cordierite disappeared and transformed to  $\alpha$ -cordierite completely, and simultaneously some amount of gahnite and a trace of quartz appeared. With increasing temperature from 950 to 1000 °C, the diffraction intensity of  $\alpha$ -cordierite gradually decreased and the diffraction intensity of gahnite accordingly increased, and the diffraction intensity of quartz was fixed on the whole. Whereas sample Z8 heat-treated at 1050 °C, the main crystalline phase was gahnite and the secondary phases were  $\alpha$ -cordierite and quartz. The changes of the crystalline phases with the temperature certainly affect the following physical properties of the glass-ceramics.

Fig. 6 presents the correlations between the dielectric property of sintered sample Z8 and sintering temperatures. Some of

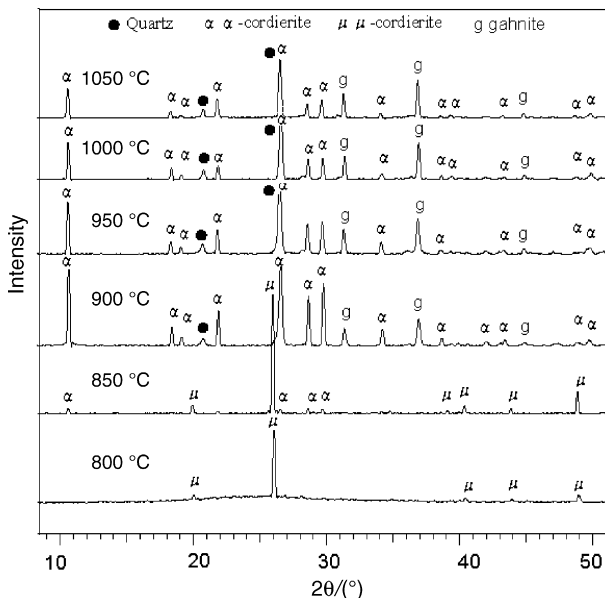


Fig. 5. XRD patterns of sample Z8 sintered at various temperatures.

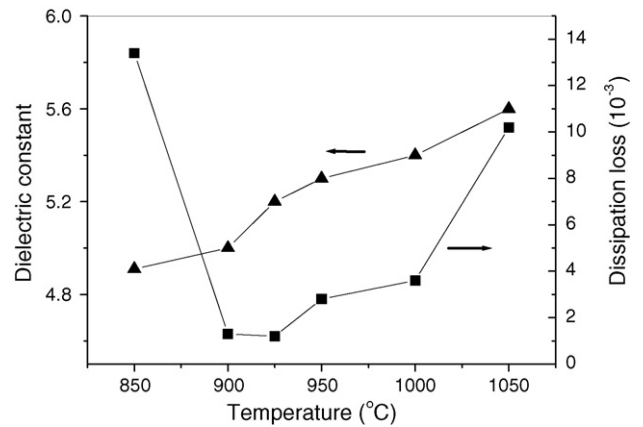


Fig. 6. Dielectric properties of sample Z8 sintered at different temperatures.

the other important properties are listed in Table 2. It is observed that the dielectric constant of sample Z8 increases with increasing sintering temperature. The dielectric loss of sample Z8 sintered at 900 and 925 °C reaches the lowest value. Dielectric properties were found to be depended upon the relative density, the type of crystalline phases and its content [21–22]. The thermal expansion coefficient of glass-ceramics chiefly depends on its crystalline phases. The flexural strength of glass-ceramics mainly depends on its relative density [23]. The flexural strength of sample Z8 firstly increases and then slightly decreases with sintering temperatures as shown in Table 2, which closely corresponds to the relative density as seen in Fig. 3. It is clear that sample Z8 sintered at 900–925 °C has the best dielectric property, and is preferred as the material for LTCCs. Firstly, it possesses the lowest dielectric loss lower than 0.0013 at 1 MHz, which is

Table 2  
Some properties of sample Z8 sintered at different temperatures

Sintering temperature (°C)	Linear shrinkage (%)	TCE ( $\times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ ) (20–300 °C)	Flexural strength (MPa)
850	11.2	5.00	62
900	18.2	4.07	125
925	18.5	4.15	135
950	18.1	5.04	121
1000	17.9	5.27	116
1050	18.0	5.82	118

desirable for reducing heat generation at high frequency. Secondly, its low dielectric constant (5.0–5.2), which is lower than that of alumina ( $\sim 9$ ), is absolutely necessary to reduce the propagation delay and parasitic capacitance ( $C_p$ ) between internal conductor patterns of LTCCs and to achieve the requirements of high signal propagation speed. Thirdly, it possesses a low thermal expansion coefficient (TCE,  $4.0\text{--}4.2 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ), very close to that of Si ( $3.0\text{--}3.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ) and a higher flexural strength. Lastly, its low sintering temperature ( $<950 \text{ }^\circ\text{C}$ ) enables the usage of Ag and Cu electrodes.

#### 4. Conclusions

The sintering and crystallization behaviors for MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system glass-ceramics containing ZnO were investigated. The replacement of Al<sub>2</sub>O<sub>3</sub> by ZnO can lower the melting temperature and crystallization temperature of the glass-ceramics. However, the glass transition temperature firstly decreased and then increased with the replacement of Al<sub>2</sub>O<sub>3</sub> by ZnO. An optimized sintering profile for glass powder containing 8 wt.% ZnO was established. After complete sintering, the fully dense glass-ceramic with crystallized  $\alpha$ -cordierite and gahnite was successfully fabricated at relative low temperature ( $<950 \text{ }^\circ\text{C}$ ). Superior and reliable properties such as low temperature sinterability, thermal expansion coefficient, flexural strength and dielectric properties at 1 MHz were successfully derived in the dense specimen prepared from MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system glass-ceramic powder containing 8 wt.% ZnO content.

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