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Low temperature sintered cordierite ceramics from MgO-Al_2O_3-SiO_2 glass powder

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ABSTRACT

Cordierite ceramics are widely used in electronic and information fields due to their excellent electrical, thermal and mechanical properties. In the present work, cordierite ceramics with both low coefficient of thermal expansion (CTE) and high flexural strength were successfully derived from MgO-Al_2O_3-SiO_2 glass powder. The effects of sintering temperature on phase composition and microstructure of the ceramics were elaborated, while the relationships among sintering temperature, CTE, mechanical strength and density were comprehensively discussed. It has been shown that the MgO-Al_2O_3-SiO_2 glass powder can be well sintered into cordierite ceramics at temperatures in the range of 1050-1150°C, which are much lower than the commonly reported sintering temperatures that are over 1400°C. Specifically, the cordierite ceramic sample sintered at 1150°C exhibits a CTE of 2.123×10^{-6} $°C^{-1}$ and a flexural strength of 97.05 MPa.

Keywords: *Cordierite ceramic; Glass powder; Low temperature sintering; Coefficient of thermal expansion.*

1. INTRODUCTION

As a new type of microwave dielectric materials, cordierite ($2MgO\cdot2Al_2O_3\cdot5SiO_2$) and cordierite-based ceramics have a wide range of applications in electronic and information industries, duo to their low coefficient of thermal expansion (CTE), low dielectric loss and excellent mechanical properties [1, 2]. However, the sintering temperature for cordierite ceramics is rather high, which is usually higher than 1400°C, when using the conventional ceramic processing method. In some cases, to obtain cordierite ceramics with desired performances, it is even necessary to use a sintering temperature that is close to its melting point. More recently, crystallization form MgO-Al_2O_3-SiO_2 glass has become a new method to fabricate cordierite ceramics [2, 3]. However, although the cordierite ceramics obtained in this way have a very low CTE, the flexural strength is generally also low, which is attributed to the presence of large number of fine cracks in the matrix [4, 5]. By modifying the composition, cordierite glass-ceramics can be developed, with flexural strengths of higher than 180 MPa [6, 7], but other phases, such as spinel and quartz, would be inevitably generated [6], thus leading to a significant increase in CTE. Additionally, sol-gel method [8] and tape casting process [1, 9] have also been used to prepare cordierite ceramics. However, the addition of large amount of organic compounds is inevitable, which not only increased the costs but also produced potential hazards to the environment.

In the present work, combining the advantages of the conventional sintering and glass crystallization methods, we have fabricated dense cordierite ceramics with low CTE and high mechanical strength at relatively low sintering temperatures, thus providing a new way to realize the industrialized production of high performance cordierite ceramics.

2. EXPERIMENTAL SECTION

2.1. Raw Materials and Chemical Composition. Chemical composition of the sample was determined according to the ternary phase diagram of MgO-Al_2O_3-SiO_2. According to previous experiments, the optimized compositions of raw materials for the sample are listed in Table 1. Kaolin was purchased from Suzhou Kaolin Co., Ltd. in China, with contents of SiO_2 and Al_2O_3 to be 46.2 wt.% and 39.1 wt.%, respectively. CaO and SiO2 were introduced with $CaCO_3$ and quartz sand, whereas other oxides were industrial raw materials. Kaolin was used to reduce the cost of raw materials, while TiO_2/ZrO_2 would promote crystallization of the glass matrix.

2.2. Sample Preparation. Batches of about 200 g were thoroughly mixed for 2 h in corundum containers with a planetary ball mill. The glass batches were melted in corundum crucibles at 1520°C for 3 h in air to obtain homogeneous glass melts. Then, they were quenched by pouring into water, followed by drying, grinding and sieving through a 200 mesh sieve.

Table 1. Composition of matrix glass (wt.%)

Composition	Kaolin	SiO_2	TiO_2+ZrO_2	CaO+MgO
Content (wt.%)	74.32	11.27	7.13	7.29

An arboxymethyl cellulose (CMC) solution with a concentration of 6.0 wt.% was used as binder, whose content was about 0.5 wt.%. The ground glass powders were pressed into strips with dimension of 10×10×40 mm3 at a pressure of 20 MPa. To prevent the samples from cracking, the green bodies were heated at 300°C for 1 h to remove the residue water and CMC. Cordierite ceramic samples were obtained by further sintering at 950-1300°C for 1 h at an interval of 50°C.

2.3. Characterization. Characteristic temperatures of the glass samples were analyzed by using a differential scanning calorimeter (DSC, model Netzsch STA-449C, Germany) at a heating rate of 5°C /min from 25 to 1200°C. Crystalline phases of the ceramics were examined by using a D/Max-2500 diffractormeter with nickel-filtered Cu/Ka radiation over a scanning angle range of 5° - 80°. The obtained samples were polished, etched with 4.0 vol.% HF solution for 60 s, cleaned with ultrasonication, coated with gold and characterized by using scanning electron microscope (SEM, JSM-6700F).

CTEs of the sintered ceramics were measured by using a thermal mechanical analyzer (Model: DIL-402PC, Netzsch, Germany) at a heating rate of 5°C/min from 25 to 800°C. Bulk density of the sintered ceramics was determined by using the Archimedes' method with a DA-600M model density meter. An electronic universal testing machine (Model: WDW-100, Letry, China) with a span of 20 mm was employed to measure flexural strength of the samples.

3. RESULTS SECTION

3.1. DSC analysis. Figure 1 shows DSC curve of the matrix glass. The glass exhibits a transition temperature (T_g) of about 661°C and a crystallization temperature (T_p) of 1061°C, which are similar to those of the $MgO-Al_2O_3-SiO_2$ systems reported previously [6]. Noting that the initial temperature for crystallization (T_i) is 958°C, the difference between T_p and T_i is more than 100°C, indicating that the matrix glass has a good crystallization stability [10]. It is worth mentioning that a weak shoulder peak is also observed at 1013°C, which is attributed to the stacking of multiple crystallization peaks, suggesting the formation of multiple crystal phases in the matrix glass. Based on the characteristic temperatures of the matrix glass, the sintering temperature should be higher than 958°C. In order to optimize the sintering temperature, a wide temperature range from 950-1300°C at an interval of 50°C was used for the experiments.

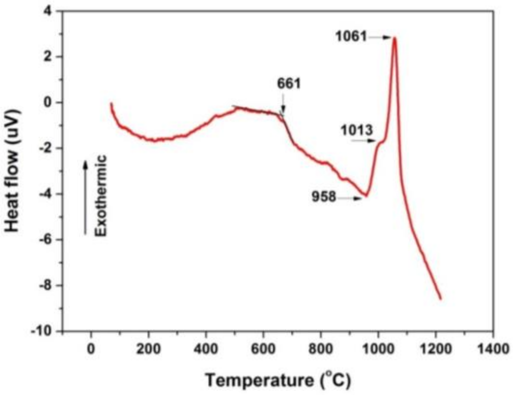

Figure 1. DSC curve of the matrix glass.

3.2. Crystallization behavior and microstructure. Figure 2 shows XRD patterns of the samples sintered at different temperatures. As expected, there are no any sharp diffraction peaks in the sample sintered at 950°C (Figure 2A), revealing amorphous nature of the sample, which is in agreement with the DSC curve. When the sintering temperature was increased to 1050°C, all typical diffraction peaks associated with cordierite ($2MgO·2Al_2O_3·5SiO_2$ or $Mg_2Si_5Al_4O_{18}$) are present (Figure 2B). The sharp diffraction peaks with gradual increase in intensity indicate the increase in crystallinity of cordierite with increasing temperature (Figure 2C). Meanwhile, a new crystal phase $ZrSiO_4$ is formed in the sample sintered at 1250°C (Figure 2D).

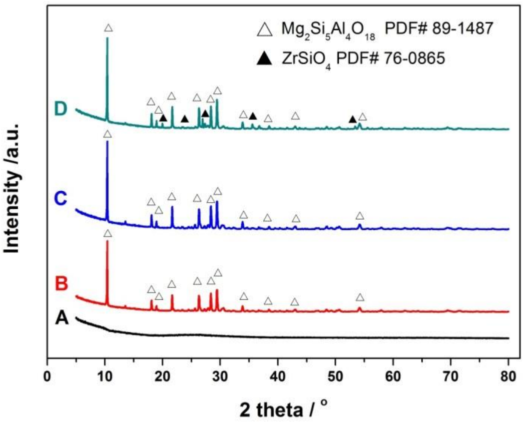

Figure 2. XRD diffraction patterns of the ceramics sintered at 950°C (A), 1050°C (B), 1150°C (C), and 1250 °C (D).

It is well known that the CTE of cordierite crystal is very low. Its CTE along c-axis is only $-1.11×10^{-6}$ $°C^{-1}$, while those along a-axis and b-axis are from $2.20×10^{-6}$ $°C^{-1}$ to $2.80×10^{-6}$ $°C^{-1}$ [11]. Therefore, cordierite based ceramics usually have a relatively low CTE than other oxide ceramics. Moreover, the CTE value can be further decreased to $0.30×10^{-6}$ $°C^{-1}$ by using the crystal orientation technology when employing extrusion molding process to obtain green bodies [12]. However, because of its high CTE, the formation of $ZrSiO_4$ crystals is not conducive to the reduction of CTE of the samples.

Figure 3 shows representative SEM images of the ceramic samples. A large number of fine crystals with size of 50 nm can be observed in the ceramic sample sintered at 1050°C (Figure 3A).

Although some of the crystals are agglomerated, most of them are evenly distributed in the matrix. Based on the XRD results, these particles are obviously cordierite crystals. As the sintering temperature is increased to 1250°C, the grains grow significantly, with an average size to more than 100 nm (Figure 3B). At the same time, the number of grains is also obviously increased, so that the matrix glass phase almost disappears. It is noteworthy that some fine cracks can also be observed in the sample (marked with arrows), which might be resulted from the excessive growth of the grains, because of different CTEs along different crystal axis.

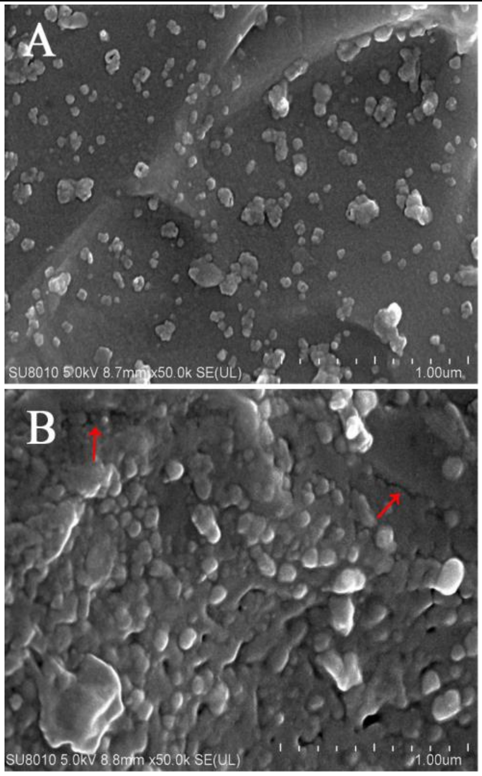

Figure 3. SEM images of the ceramics sintered at 1050°C (A) and 1250°C (B).

3.3. Physical Properties. Thermal expansion behavior of cordierite ceramics is the most concerned parameter for their applications in the fields of electronic and information industries. A small dimensional variation caused by thermal expansion or contraction will have a significant negative affect on the performance of the products. Flexural strength is also an important indicator, which usually determines processing performance and service life of the ceramics. In the present work, CTE, flexural strength and bulk density of the ceramic samples sintered at different temperatures are systematically characterized, with all the data to be listed in Table 2.

Figure 4 shows CTE of the ceramic samples as a function of sintering temperature. With increasing sintering temperature, the CTE has a rapid decrease from 950°C to 1050°C and then a slow increase after 1100°C. The CTE of the sample sintered at 950°C is 4.93×10^{-6} $^{\circ}C^{-1}$, which is much higher than those of the ones sintered at 1000-1300°C. According to the DSC and XRD results, the sample sintered at 950°C is still in amorphous state, containing no crystalline phase, The CTE value is in good agreement with that of MgO-Al_2O_3-SiO_2 glass. After sintering at 1000°C, the CTE rapidly drops to 2.27×10^{-6} $^{\circ}C^{-1}$. This is because the sintering temperature is higher than the initial temperature for crystallization, so that cordierite crystal is formed and thus a lower CTE is observed. As the sintering temperature is increased to 1050°C, the lowest CTE of 1.96×10^{-6} $^{\circ}C^{-1}$ is achieved. This is mainly attributed to the fact that a large number of fine cordierite crystals are distributed evenly in the matrix of the sample. However, the CTE begins to rise after sintering at 1050°C. When the sintering temperatures are higher than 1200°C, the rising trend is significantly pronounced. The CTE reaches 2.91×10^{-6} $^{\circ}C^{-1}$ when the sintering temperature is 1300°C, which is about 1.5 times that of the sample sintered at 1050°C.

According to the XRD patterns of the samples, the formation of the $ZrSiO_4$ crystals should be responsible for the high CTE of the sample sintered at the highest temperature. This is simply because $ZrSiO_4$ crystal has a theoretical CTE of 5.63×10^{-6} $^{\circ}C^{-1}$[13] and an experimental value of 4.65×10^{-6} $^{\circ}C^{-1}$ [14], which are much higher than that of cordierite crystal.

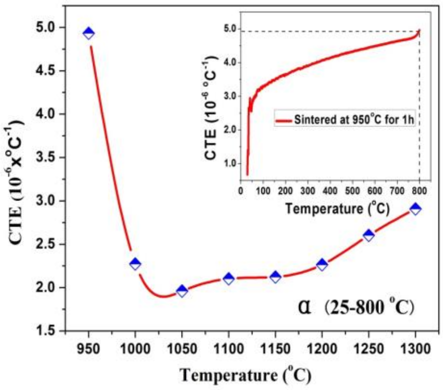

Figure 4. CTE of the cordierite ceramics as a function of sintering temperature.

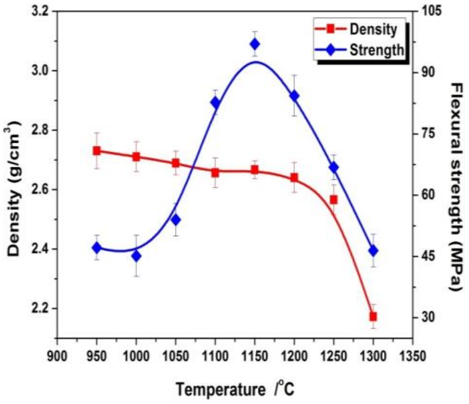

Figure 5. Density and strength of the cordierite ceramics as a function of sintering temperature.

Table 2. Physical performances of the cordierite Ceramic sintered at different temperatures.

Sintered Temperature (°C)	950	1000	1050	1100	1150	1200	1250	1300
CTE (10^{-6} °C^{-1})	4.93	2.27	1.96	2.10	2.12	2.27	2.60	2.91
Density (g/cm^3)	2.73	2.71	2.69	2.66	2.67	2.64	2.57	2.17
Strength (MPa)	47.19	45.18	54.03	82.78	97.05	84.38	66.86	46.47

Figure 5 shows flexural strength and bulk density of the samples as a function of sintering temperature. It is observed that flexural strength of the samples is increased firstly then decreased with increasing sintering temperature. The sample sintered at 1150°C has the highest flexural strength of 97.05 MPa. In fact, as a ceramic material based on MgO-Al_2O_3-SiO_2 system, this strength value is not very high. Ceramic materials based on this system with flexural strength even higher than 300 MPa have been reported [6]. However, those ceramics usually have CTEs of higher than 4×10^{-6} °C^{-1} [6, 15, 16], which cannot be considered to be low CTE materials. The sample sintered at 950°C has a flexural strength of only 47.19 MPa. Obviously, the flexural strength can be improved by increasing the sintering temperature, due to the formation and growth of the cordierite crystals. However, as the sintering temperature is higher than 1150°C, the excessive growth of the crystals and the secondary recrystallization result in formation of a large number of fine cracks in the samples (Figure 3B), thus leading to reduction in flexural strength. The variation trend in flexural strength is well consistent with that in bulk density of the samples. The samples sintered at temperatures of lower than 1150°C have almost the same density, which indicates that the compaction degree of samples is high stable. In this case, the increase in crystallization from the glass matrix results in a monotonous increase in flexural strength. As the temperature is higher than 1150°C, the formation of the cracks lowers the structural compaction, so that the bulk density is rapidly reduced.

4. CONCLUSIONS

It is generally difficult to obtain cordierite ceramics with low CTE and high flexural strength at the same time when using the ordinary synthetic processes. In this study, a unique method has been demonstrated to develop cordierite ceramics from $MgO-Al_2O_3-SiO_2$ glass, which exhibit lower CTE and higher strength than those made with the common synthesis technologies. Moreover, the sintering temperature is significantly lower than that required when using the normal process for cordierite ceramics. The optimal sintering temperature is within the range of 1050-1150°C. The sample sintered at 1050°C has the lowest CTE of 1.960×10^{-6} °C^{-1}, while the one sintered at 1150°C possesses a maximum flexural strength of 97.05 MPa. We believe that this technology can be readily used for large-scale production of cordierite ceramics for industrial applications.

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6. ACKNOWLEDGEMENTS

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