Solid state synthesis and its characterization of high density cordierite ceramics using fine oxide powders

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First, we succeeded in synthesizing and sintering cordierite ceramics via the solid state reaction route without the melting process by using single phase oxide powders. They are highly pure and fine amorphous silica, α -alumina and magnesia powders. Usually, cordierite ceramics was synthesized by a sol–gel route. Alternatively, it was prepared by a solid state reaction route using impure minerals such as talc, or the other which required melt-quenching and crystallization processes, though using single phase raw material powders. This is probably because single phase raw material powders especially alumina are deficient in reactivity. We have succeeded in synthesizing cordierite ceramics via the solid state reaction route without melt-quenching and crystallization processes, by adopting a reactive α -alumina as one of raw material powders. As a result, cordierite formation of the starting raw material mixture went to completion at 1270°C. The mixture was sintered at 1430°C for 2 h. Its bulk density reached 98% theoretical, its flexural strength reached 243 MPa, which agreed with the best value already reported, its fracture toughness was 3.5 MPa·m^{1/2} far larger than the reported value of 2.3 MPa·m^{1/2}, its thermal expansion coefficient (from RT. to 800°C) is 1.8×10^{-6} /K, which might be probably the ultimately smallest value experimentally expected and its dielectric constant was sufficiently small as 4.8 to 5.2 between extremely a wide frequency range, namely, from 1 MHz to 1 GHz with low loss tangent of < 6×10^{-3} . These properties were found more excellent or at least comparable compared with the best properties reported already and suitable for substrate materials on micro-electronic applications.

Key-words : Synthesis, Cordierite, High purity oxide, Solid state reaction route, Physical properties, High density

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1. Introduction

The phase diagram of cordierite was first reported by Rankin and Merwin on the ternary system MgO-Al₂O₃-SiO₂.¹⁾ Cordierite ceramics is one of the candidates as a substrate material for microcircuit applications in electronic fields due to its low thermal expansion coefficient and low dielectric constant. Also, it has been utilized as a ceramic honeycomb for a catalystic support in an automobile exhaust system. However, it is difficult to obtain dense cordierite ceramics by the sintering process because its sintering temperature range is limited within 25°C below its melting point of 1455°C.²⁾ Many previous studies were reported about the sinterability of cordierite ceramics. Recently, dense cordierite ceramics have been produced at low temperature by the sol-gel method using alkoxides of Si and Al.³⁾ However, the starting materials via this method are very expensive and the fabrication processes are complicated. In addition, the properties of the obtained ceramics were not excellent compared with those reported already.4),5)

Alternatively, cordierite ceramics were prepared by a solid state reaction route using impure minerals such as talc,⁶⁾ or the other which required melt-quenching and crystallization processes, though using single phase raw material powders.⁷⁾ The properties of both sintered ceramics were also insufficient compared with those reported already.^{4),5)}

This paper aims to synthesize cordierite ceramics by the conventional solid state reaction without melt-quenching and crystallization processes using highly pure, fine and reactive oxide powders. In addition, it aims to obtain highly densified cordierite ceramics with enhanced properties.

2. Experimental

The starting raw oxide powders were used high purity Magnesia (Soekawa Chemical Co., Ltd., 99.99%), α-alumina with an average diameter of 0.1 µm (TM-DAR, Taimei Chemicals Co., Ltd., 99.99%), and amorphous Silica (Kanto Chemical Co., Inc., 99.9%). Magnesia powder was heated at 900°C for 2 h to remove magnesium carbonate. These raw material powders are expected to react with each other at low temperatures. Especially, TM-DAR is prepared by thermally decomposition of aluminum dawsonite {NH₄AlCO₃(OH)₂} so that it is highly reactive compared with the other commercially available α -alumina. The starting mixture with a stoichiometric composition of cordierite $(MgO:Al_2O_3:SiO_2 \text{ molar ratio} = 2:2:5)$ was prepared from these oxide powders. The powders were mixed in a planetary ball mill (Itoh Industry Co., Ltd.) using zirconia balls of 3 mm in diameter in isopropyl alcohol (IPA) for 3 h, added with 1% of poly vinyl butyral (PVB). After drying, the mixture was pressed in a die at a pressure of 30 MPa, CIPed at a pressure of 200 MPa, and heattreated in air for 2 h from 1100°C to 1350°C to examine reaction procedure of the compact of the mixture and determine proper calcining temperature of the mixture for its sintering. The scanning electron microscope (SEM) observations for the powders and the cross section of the sintered samples were carried out using an SEM instrument (JSM-5200, JEOL Ltd.). Crystalline phases in the heat-treated samples were identified by XRD

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(RINT 2000, Rigaku Co.) using Cu K α radiation. Bulk density of the sample was determined by the liquid displacement method using water, namely Archimedean method. Flexural strength of the sample was evaluated by the three point bending experiment and Young's modulus was estimated from the stress-strain curve during the experiment. The values of Vichers hardness and fracture toughness were obtained from the indentation process and IF method.⁸⁾ Differential scanning calorimetry (DSC) of the green compact was performed employing a Rigaku DSC 8270 equipment at a heating rate of 5 K/min and thermal expansion coefficient of the sample was measured using a dilatometer (TMA 8310, Rigaku Co.). Dielectric constants were estimated from the values of the capacitance measured at 1 MHz and 1 GHz using impedance analyzers (YHP4192A and 4191A, Yokokawa-Hewlett-Packard Co.), respectively.

3. Results and discussion

Figure 1 shows representative DSC plots of the compact of



Fig. 1. Representative DSC plot for the compact of the starting mixture.



Fig. 2. XRD patterns for the compact of the starting mixture heattreated at various temperatures for 2 h. A: Corundum, M: MgO, F: Forsterite, C: Clinoenstatite, Sp: Spinel, E: Enstatite, β -Qss: β -Quartz solid solution, Cr: Cristobalite, Sa: Sapphirine, a: α -Cordierite.

the mixture. As seen, a sharp exothermic peak at 1181°C and three endothermic peaks at 1175°C, 1422°C and 1462°C are observed. The sharp exothermic peak at 1181°C can be assigned to crystallization of cordierite from β -quartz solid solution (β -Qss), cristobalite and sapphirine on the basis of XRD patterns shown in **Fig. 2**. The first endothermic peak at 1175°C that begins at 1160°C corresponds to formation of β -Qss with cristobalite and disappearance of a broad diffraction peak at around $2\theta = 21.8^\circ$, which corresponds to amorphous silica shown in Fig. 2. The second peak at 1422°C corresponds probably to libration of silanol radicals from silica. The last peak at 1462°C is assigned to the melting of cordierite.

Figure 2 shows XRD patterns of the compact of the mixture heat-treated at 1100–1270°C for 2 h. In the pattern for the compact of the mixture heat-treated at 1100°C, peaks of forsterite, clinoenstatite, corundum and weak peak of magnesia, a broad diffraction peak of amorphous silica at around $2\theta = 21.8^{\circ}$ are observed. This result indicates that all magnesia reacts with a part of amorphous silica to form forsterite and clinoenstatite below 1100°C. At this temperature, corundum remains unreacted. At the narrow temperature range from 1150°C to 1180°C, a considerable change in XRD patterns is observed. The weak peaks of spinel and enstatite appear and the peaks of forsterite



Fig. 3. SEM photograph of the pulverized powder.



Fig. 4. Bulk density of the sample sintered as a function of sintering temperature.



Fig. 5. SEM photographs of the cross sections for the samples sintered at various temperatures. (a) 1300°C, (b) 1350°C, (c) 1400°C, (d) 1430°C and (e) 1450°C.

and clinoenstatite vanish at 1150°C. At 1160°C, the peak of β quartz solid solution appears accompanied by the disappearance of a broad diffraction peak of amorphous silica. Cristobalite, sapphirine and cordierite appear at 1170°C with decrease in the peak intensity of the β -quartz solid solution. At 1240°C, the main crystal phase is α -cordierite with a weak diffraction peak of spinel. Finally, only α -cordierite phase is observed for the compact of the mixture heat-treated above 1270°C. Accordingly, the proper calcination temperature of the raw material mixture was determined as 1240°C. It was the lowest temperature at which sintering process of the mixture was expected to proceed easily.

First, the mixture was calcined at 1240°C for 2 h and then pulverized in a planetary ball mill using zirconia balls of 3 mm in diameter in IPA for 6 h. Next, it was pulverized again for 48 h in a usual ball mill also using zirconia balls of 3 mm in diameter in IPA containing a surfactant (Kusumoto Chemicals) and dried. The pulverized powder was added with 1% of PVB, pressed in a die at a pressure of 30 MPa, CIPed at a pressure of 200 MPa to form its compact. The compact was sintered in air from 1350°C to 1450°C for 2 h, respectively. As seen, from the SEM photograph in Fig. 3, the grain size of the pulverized powder is about 0.5 μ m, indicating that sufficiently fine pulverization was attained. Figure 4 shows bulk density of the sintered sample as a function of sintering temperature. It increases with increasing sintering temperature, reaches a maximum of 2.53 g/cm³ at 1430°C and decreases to 2.49 g/cm³ at 1450°C. The true density of the sample sintered at 1430°C was determined as 2.59 g/cm³ by the conventional pycnometer method. Accordingly, a sufficiently high densification of 98% was attained at 1430°C sintering. Figure 5(a) to (e) show SEM photographs of the cross sections for the samples sintered at various temperatures. As visually observed, the sample density increases with increasing temperature and almost complete densification is attained at 1430°C sintering. However, many porous regions are observed in the matrix for the sample sintered at 1450°C probably due to the libration of silanol radicals contained in amorphous silica. This phenomenon corresponds to the decrease in bulk density and the endothermic peak observed at 1422°C in Fig. 1.

In addition, **Fig. 6** shows flexural strength of the sintered sample as a function of sintering temperature. It increases with increasing sintering temperature, reaches a maximum of 243 MPa at 1430°C and decreases to 200 MPa at 1450°C. This behavior agrees with exactly that of the bulk density, described



Fig. 6. Flexural strength of the sintered sample as a function of sintering temperature.

above.

Table 1 summarizes the values of thermo-mechanical and electrical properties of our sample sintered at 1430°C with the standard values previously reported,^{4),5)} respectively. As seen in the Table, all the values of the properties for the sintered sample are comparable or at least prominent compared with the values of the standard sample. It is noted that the latter values are the best values collected from various sources. First, the value of Vichers hardness is a little smaller than the standard value. Next, the value of flexural strength agrees with the standard value. The value of Young's modulus enhanced twice the standard value. The value of fracture toughness is 3.5 MPa·m^{1/2} far larger than the standard value and comparable that of alumina = $4.0 \text{ MPa} \cdot \text{m}^{1/2}$. The coefficient of thermal expansion is a little larger than the standard value, which was theoretically evaluated by Evans et al^{4),9)} from temperature dependence of the lattice constants of cordierite. Therefore, this value may be probably the ultimate one practically obtained. The value of dielectric constant 4.8 (at 1 MHz) -5.2 (at 1 GHz) is almost the same as the standard value

Table 1.	Thermo-mechanical	and	Electrical	Properties	of	Sin-
tered Samples						

Properties	Our sample	Standard ^{4),5)}		
Sintering temperature (°C)	1430			
Bulk density (g/cm ³)	2.53			
Vickers hardness (GPa)	7.5	8.2		
Flexural strength (MPa)	243	245		
Young's modulus (GPa)	281	139		
Fracture toughness (MPa·m ^{1/2})	3.5	2.3		
Coefficient of thermal expansion	1.8	1 59)		
(× 10 ⁻⁶ /K) (RT.–800°C)	1.0	1.5		
Dielectric constant (1 MHz)	4.8	5.0		
(1 GHz)	5.2			
Loss tangent (1 MHz, $\times 10^{-3}$)	1.2			
$(1 \text{ GHz}, \times 10^{-3})$	6.3			

True density of our sample = 2.59 g/cm^3 .

of 5.0 with low loss tangent of $< 6 \times 10^{-3}$ even at 1 GHz. It should be noticed that the value remains constant independent of the frequency over extremely wide frequency range. On the other hand, dielectric constant of the sample prepared by a sol–gel route¹⁰⁾ decreases with increasing frequency even at MHz region probably due to imperfectness in the sample, though the value at 1 MHz is almost the same. Furthermore, it is considerably low that of alumina = 9.5.^{4),5)} These experimental results indicate that the sample can be applicable as a substrate material for microelectronic devices.

4. Conclusion

Synthesis of cordierite ceramics was attained using high purity

and fine oxide powders by solid state reaction and fabrication of high dense cordierite ceramics was also attained. Cordierite formation for the starting raw material mixture went to completion at 1270°C. The density of the sample sintered at 1430°C reached 98% of the true density. In addition, its flexural strength was enhanced to 240 MPa, which is almost the same as that of standard value. Coefficient of thermal expansion $(1.8 \times 10^{-6}/\text{K})$ and dielectric constant (4.8 at 1 MHz) are also almost the same as that of standard value. In addition, dielectric constant remains constant independent of the frequency over extremely wide frequency range from 1 MHz to 1GHz with loss tangent of < 6 × 10⁻³. As a conclusion, high density and outstanding characteristics cordierite ceramics was obtained by using simple powder mixing method without using complex sol–gel method.

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