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# Preparation of dense cordierite ceramics from magnesium compounds and kaolinite without additives

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## Abstract

Thermal reactions of magnesium compounds and kaolinite were investigated to obtain dense cordierite ceramics without additives. Magnesium hydroxide was precipitated from aqueous solution in the form of ultrafine hexagonal tabular particles of about 0.1 μm, and heating this mixture with submicron particles of tabular kaolinite in a molar ratio of $MgO{\cdot}Al_2O_3{\cdot}2SiO_2$ resulted in the formation of an amorphous state at about 900°C after thermal decomposition. μ-Cordierite was then crystallized from the amorphous phase at about 950°C, and gradually transformed into α-cordierite from 950 to 1200°C. Firing the pressed specimens at 1350°C yielded a dense α-cordierite ceramics with a relative density higher than 95% and a negligible open porosity, and it showed a linear thermal expansion coefficient of $2.2{\times}10^{-6}$/K. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

*Keywords:* A. Sintering; C. Thermal expansion; D. Cordierite; E. Substrate

## 1. Introduction

Cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) ceramics have excellent thermal shock resistance due to their low thermal expansion, and are often used as honeycomb-shaped catalyst carriers in automobile exhaust systems. In addition, cordierite is expected to have great potential as a substrate material for integrated circuit boards [1] replacing alumina, which has a relatively lower dielectric constant at the high frequency region. In recent years, dense cordierite ceramics [2,3] and high strength cordierite/mullite composites [4] have been produced by the sol–gel method using alkoxides of Si and Al. Although dense cordierite ceramics can be obtained from alkoxides at low temperature, the starting materials are very expensive and the fabrication processes are complicated. Despite the numerous attempts and extensive research, kaolinitic materials have not been successfully used to produce dense ceramics consisting of α-cordierite except for our previous research [5].

In this study, ultrafine particles of magnesium hydroxide were precipitated from aqueous solution of reagent grade magnesium chloride, and dense α-cordierite ceramics were obtained by mixing these particles with elutriated submicron kaolinite and by firing at 1350°C for 1 h.

## 2. Experimental procedure

### 2.1. Sample preparation

GB (green bush) kaolin powders (Greenbush, West Australia, Australia), wet-classified with diameters of less than 1, 3 or 5 μm, were used as the kaolinite materials in wet-state before drying, and designated as GB1, GB3 and GB5. The particle size distribution and chemical composition of raw materials are shown in Fig. 1 and Table 1, respectively. The classified kaolin powders consist of tabular particles of kaolinite with an average particle size of 0.3, 0.8 and 1.0 μm. The alkaline metal oxide ($K_2O$, $Na_2O$) content in the kaolin was extremely low.

Ultrafine particles of magnesium hydroxide were precipitated from 200 ml of 0.25 mol/l magnesium chloride solution with 50 ml of 14.8 mol/l ammonia solution and separated by a centrifugal separator. The TEM photographs of the synthesized magnesium hydroxide and

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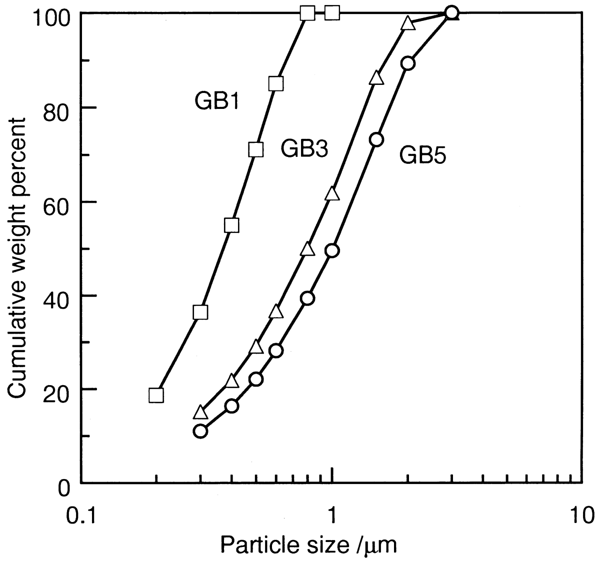

Fig. 1. Particle size distribution of GB kaolin.

elutriated kaolin are shown in Fig. 2. Magnesium hydroxide particles are the hexagonal tabular microcrystals in an average width of about 0.1 μm, and the thickness is estimated to be about 20 nm by X-ray line broadening. Magnesium hydroxide particles were mixed with the kaolinite particles in wet-state to prevent aggregation and insufficient dispersion by drying.

After weighing the magnesium compound and kaolinite in a molar ratio of $MgO{\cdot}Al_2O_3{\cdot}2SiO_2$, the mixtures were ultrasonically dispersed and gradually dried while being stirred in a mortar. The specimens were designated as GB1-M, GB3-M, and GB5-M depending on the elutriation particle size of kaolin. The mixed powders were uniaxially pressed at 98 MPa to form a disk of diameter 16 mm. The green compacts were fired in air from room temperature up to 1000°C at a rate of 5°C/min in air, and at 2.5°C/min above 1000°C. In order to examine the thermal reaction of the mixtures, compacted specimens were quenched from a specified temperature during heating. For the determination of sintering characteristics, the specimens were heat treated for 1h at respective temperatures, after which the furnace was allowed to cool down.

For the bending strength measurements, a large quantity of samples was necessary. Therefore, the mixtures of GB kaolin and magnesium hydroxide were ball-milled using alumina balls that were 10 mm in diameter and dehydrated by filter pressing. After that, cylindrical specimens were prepared by using extrusion molding.

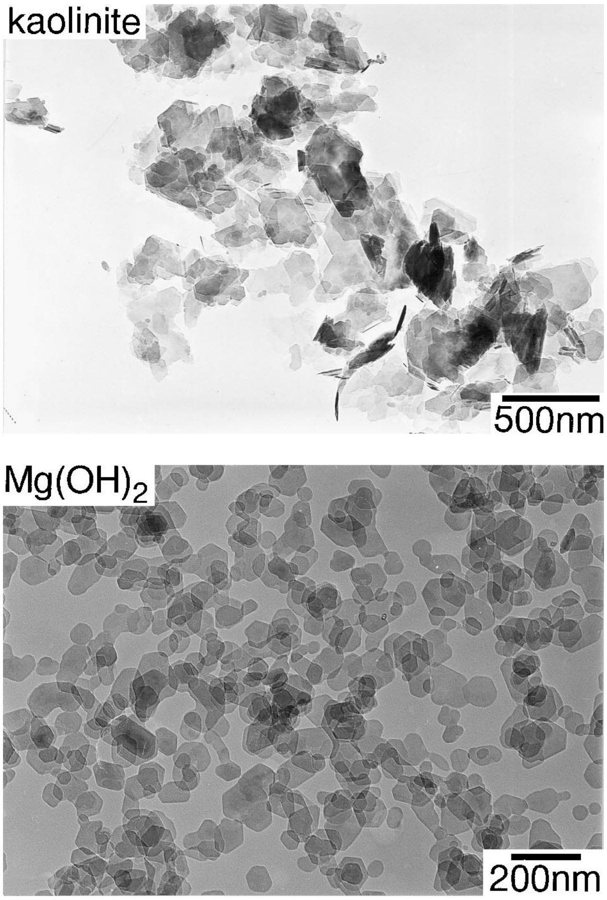

Fig. 2. TEM photographs of kaolinite and synthesized magnesium hydroxide.

Table 1
Chemical composition of GB kaolin

| Oxide | Mass% GB1 | GB3 | GB5 |
|---|---|---|---|
| $SiO_2$ | 45.68 | 45.75 | 46.46 |
| $Al_2O_3$ | 38.36 | 38.23 | 38.39 |
| $Fe_2O_3$ | 0.51 | 0.53 | 0.52 |
| $TiO_2$ | 0.01 | 0.01 | 0.01 |
| CaO | 0.05 | 0.02 | 0.01 |
| MgO | 0.27 | 0.25 | 0.23 |
| $K_2O$ | 0.01 | 0.01 | 0.01 |
| $Na_2O$ | 0.01 | 0.01 | 0.01 |
| Ig. loss | 14.76 | 14.37 | 14.33 |
| Total | 99.76 | 99.18 | 99.97 |

## 2.2. Properties measurements

The morphology of starting materials was observed by transmission electron microscope (TEM; JEOL, JEM-200-2010). Particle-size distribution was determined by a centrifugal sedimentation size analyzer (Shimazu, SA-CP3L). Crystalline phases were identified by means of X-ray diffraction (Rigaku Denki, RAD-B) with Cu*K*α radiation. X-ray intensity is determined by the diffraction peak heights using the following positions:

| Mineral | JCPDS number | (hkl) | Diffraction angle |
|---|---|---|---|
| α-Cordierite | 13-293 | (111) | 10.4° |
| μ-Cordierite | 14-249 | (100) | 19.6° |
| spinel | 21-1152 | (400) | 44.7° |
| MgO | 45-946 | (200) | 42.9° |

DTA and TG measurements were carried out using a DTA-TG apparatus (Rigaku Denki, TAS-100) at a heating rate of 10°C/min. Thermal expansion coefficient of fired specimens were measured using TMA apparatus (Rigaku Denki;TAS-100) at a heating rate of 10°C/min from 30 to 900°C. Bulk density and apparent porosity (open porosity) were determined by the Archimedes immersion technique. The fracture strength of fired specimens was measured via 3-point bending method, using cylindrical specimens.

The microstructures of the fired specimens were observed by a scanning electron microscope (SEM; JEOL, JSM-5310) on the polished and etched surface.

## 3. Results and discussion

### 3.1. Phase changes

Pressed specimens, GB1-M and GB3-M were heated and quenched at temperatures ranging from 800 to 960°C. XRD patterns of the specimens are shown in Fig. 3. In the case of GB3-M, the peak intensity of MgO decreased with increasing temperature and disappeared at 940°C. In the case of GB1-M, MgO decreased with the increase in temperature from 800 to 900°C, and completely disappeared at 920°C. In both cases, MgO disappeared before the crystallization of μ-cordierite. X-ray diffraction pattern of the specimen GB1-M fired at 1300°C for 1 h is shown in Fig. 4. α-Cordierite and a small amount of spinel were detected.

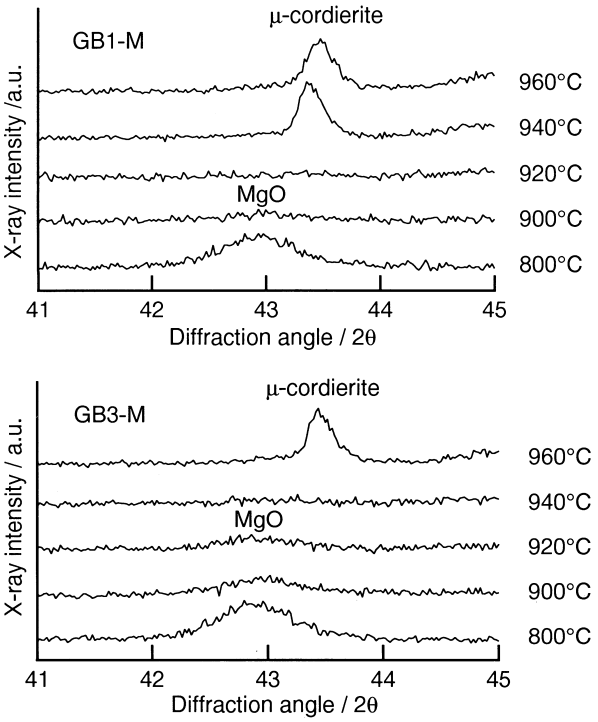

Fig. 3. XRD patterns of fired specimens.

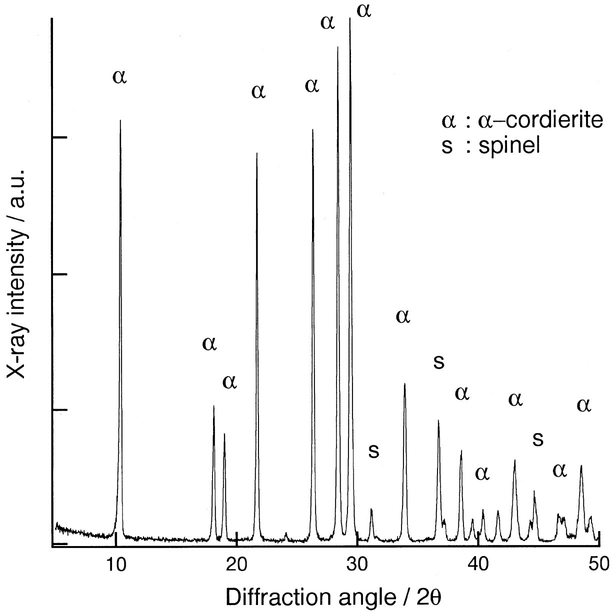

Fig. 4. XRD pattern of GB1-M fired at 1300°C.

### 3.2. Thermal analysis

The results of the DTA-TG measurement for GB1-M are shown in Fig. 5. Endothermic peaks between 350 and 400°C show the dehydration of magnesium hydroxide. The endothermic peak around 515°C represents the dehydration of kaolinite. DTA baseline shifted to the exothermic side before the crystallization of μ-cordierite, which would have been affected by abrupt sintering of the samples. The exothermic peak indicates that the crystallization of μ-cordierite occurred at about 950°C in GB1-M. Furthermore, the second exothermic peak at 1010°C corresponds to the transformation of μ- to α-cordierite. Powders derived from the sol–gel method [6] showed that the transformation temperature tended to be lower with increasing homogeneity of the precursor. We concluded that a homogeneous amorphous state in $MgO{\cdot}Al_2O_3{\cdot}2SiO_2$ composition was accomplished in GB1-M.

### *3.3. Sintering*

Bulk density and apparent porosity of the specimens fired at respective temperatures for 1 h are shown in Fig. 6. In this study, the expected mineral composition of the starting mixtures corresponded to about 89 mass% of cordierite and 11 mass% of spinel from the phase diagram [7]. True density of the fired specimens was calculated from the ideal mineral composition. Apparent porosities of all the specimens fired at 1350°C were almost zero and the relative densities were above 95.0%.

In Fig. 7, changes of crystalline phases were shown for the GB1-M fired at respective temperatures. μ-Cordierite crystallized at 900°C, and disappeared at 1000°C

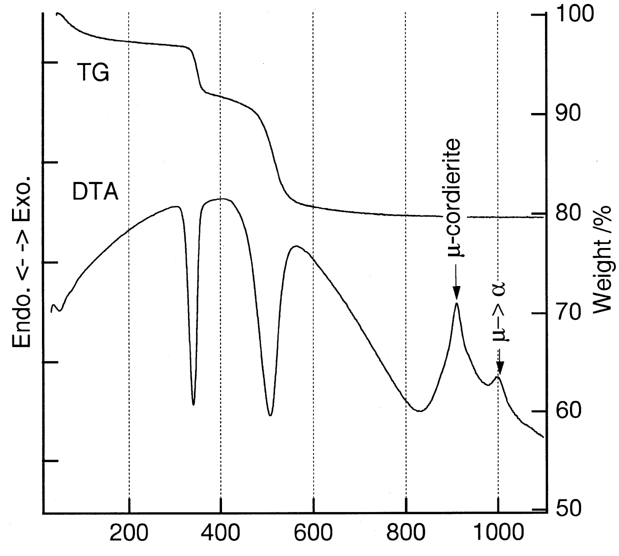

Fig. 5. DTA-TG curves of GB1-M.

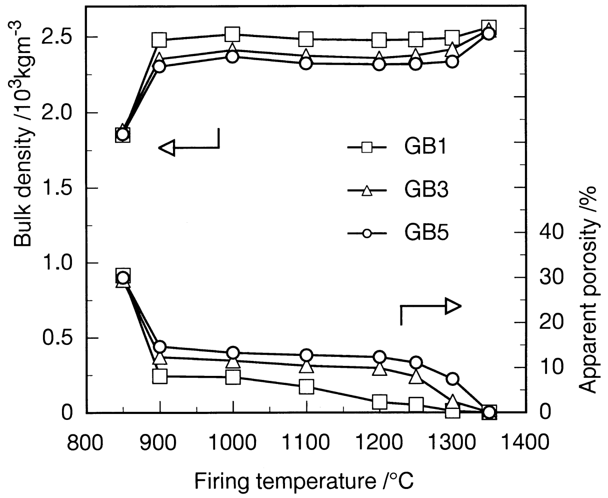

Fig. 6. Sintering characteristics of specimens.

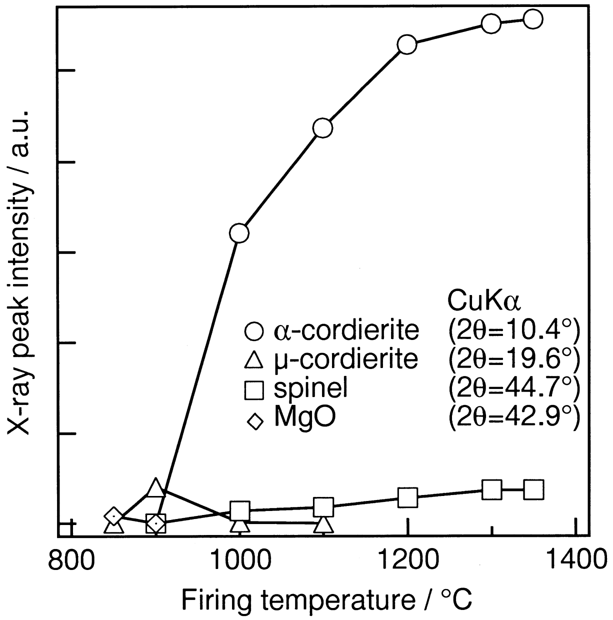

Fig. 7. Crystalline phases of fired specimens.

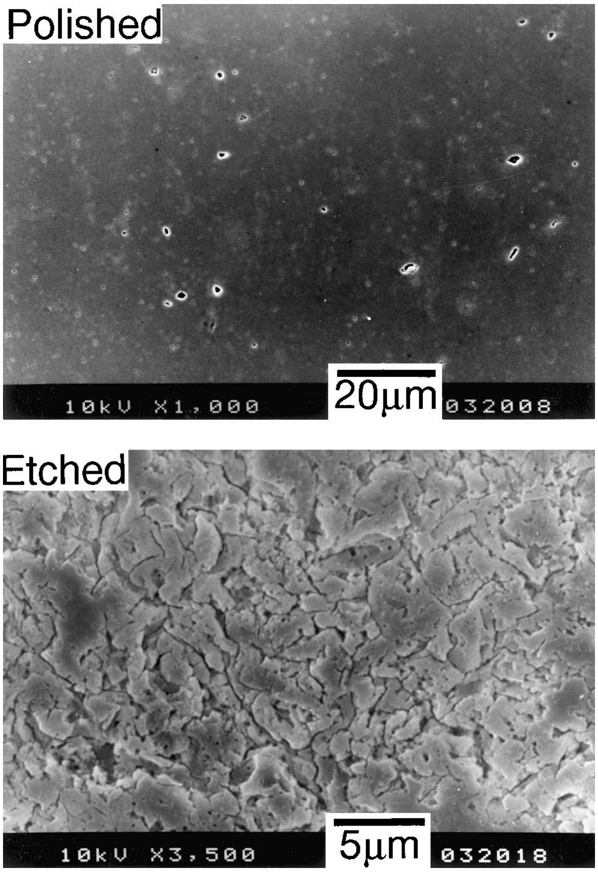

Fig. 8. S.E.M. photographs of GB3-M fired at 1350°C for 1 h, polished and etched.

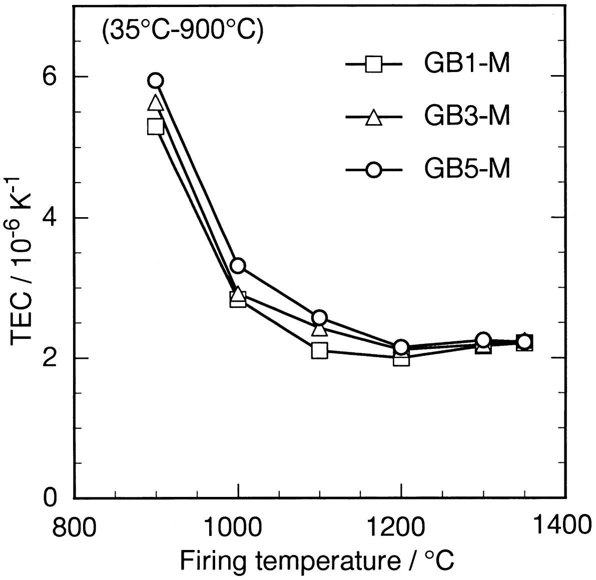

Fig. 9. Linear thermal expansion coefficient (TEC) of fired specimens.

with the advent of α-cordierite. It suggests that μ-cordierite crystals gradually transformed into α-cordierite.

SEM photographs of the polished and etched surface for the GB3-M specimen fired at 1350°C are shown in Fig. 8. The pores observed in the photo (Polished) show good agreement with the density shown in Fig. 6. Particle size of cordierite crystals was estimated as 3–5 μm from the etched surface in Fig. 8.

### 3.4. Properties

The thermal expansion coefficients (TEC) of fired specimens are shown in Fig. 9. TEC decreased with the increase of α-cordierite content and dense cordierite ceramics with thermal expansion less than $2.2\times10^{-6}$/K was obtained by firing at 1350°C for 1 h.

The fracture strengths of GB1-M fired at 1300 and 1350°C for 1 h were 164 and 175 MPa, respectively. The strength 175 MPa is sufficient for the use as substrate materials and thermal shock-resisting materials.

## 4. Conclusion

In this study, dense cordierite ceramics were obtained from the mixtures of synthesized ultrafine magnesium hydroxide and submicron particles of tabular kaolinite by firing at 1350°C for 1 h. It appears that the amorphous materials containing magnesia formed during heating at about 900°C are ultrafine and extremely sinterable. Thus produced cordierite ceramics can be expected to be utilized as substrate materials for integrated circuit boards and also as thermal shock resistance ceramics.

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