JOURNAL OF MATERIALS SCIENCE 29 (1994) 412–418

Synthesis of cordierite and cordierite–$ZrSiO_4$ composite by colloidal processing

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Cordierite powder of high purity and cordierite–ZrO_2 composite powder were synthesized by colloidal processing. Cordierite was synthesized by calcining a precursor gel obtained by gelation and coprecipitation of AlOOH sol, SiO_2 sol and $Mg(NO_3)_2$. The calcination temperature affected the constituent phases in the powders. The phase assemblage in calcined powder affected the sintering conditions. The optimum sintering temperature of the powder with cordierite single phase was 1440–1450 °C when it was calcined at 1270 °C. The sintered body had a dense microstructure with submicrometre grains. Addition of ZrO_2 sol resulted in reaction with cordierite to form mostly $ZrSiO_4$ at the sintering temperature. Several properties of cordierite and cordierite–$ZrSiO_4$ composite, such as thermal expansion coefficient, bending strength, dielectric constant and insulation properties at high temperature, were investigated. Thermal expansion and electric properties were degraded by an increasing amount of ZrO_2 additive, whereas the bending strength was improved by the addition of ZrO_2.

1. Introduction

Cordierite has been used as a thermal shock-resistant ceramic like a honeycomb for holding a catalyst at high temperature [1]. Recently, it has been suggested for use as substrate for electronic devices because of its low dielectric constant [2]. However, there is a problem for its utilization because of the difficulty of sintering it. Sintering of cordierite has been promoted under restricted firing conditions just below its melting temperature. Some attempts at improvement of the sintering properties have been made by using additives, but the use of an additive leads to inferior thermal expansion or electronic properties. The alkoxide method [3–6] is effective for improvement of the sintering process, but alkoxides are very expensive.

Sol–gel processing using a colloid mixture has been suggested for improvement of the synthesizing process and its cost performance. A heterogeneous distribution of each element sometimes promotes the sintering of bodies by the genesis of a liquid phase of lower melting temperature than that of a single phase [7]. Thus this method will be especially effective for multicomponent systems. Ismail *et al.* [8] reported colloidal processing of the mullite–cordierite system, and Travitzky *et al.* [9] synthesized a cordierite–ZrO_2 composite.

In this report, we adopted this method for the synthesis of cordierite single phase and cordierite–$ZrSiO_4$ composite to improve its sintering property and electrical, mechanical and thermal expansion properties.

2. Experimental procedure

Silica sol as a source of SiO_2 and boehmite sol as a source of Al_2O_3 were used as starting materials and mixed by stirring for 3 h. $Mg(NO_3)_2$ solution was prepared by dissolving $Mg(OH)_2$ in HNO_3 solution and then mixed with a mixture of silica sol and boehmite sol for 3 h. ZrO_2 sol of 5–30 wt % with respect to cordierite was added in the case of cordierite–$ZrSiO_4$ composite. Ammonium carbonate solution was used for the gelation by a rapid change of pH from less than 1 to above 11. $Mg(CO_3)_2$ was spontaneously precipitated and uniformly mixed with the gel. The gel obtained was filtered and dried at 90 °C for 12 h. The dry gel was calcined at 500–1400 °C for 1 h. Calcined powders were ground for 24 h by ball mill and formed into compacted bodies by uniaxial pressing followed by cold isostatic pressing (CIP) at 200 MPa. The sintering process was carried out at a temperature between 1400 and 1450 °C for 1 h (Fig. 1).

The density of each specimen was measured by the Archimedes method. The thermal expansion coefficient was measured for the range from R.T. to 1200 °C with alumina as reference. The bending strength was measured by the three-point bending test. The dielectric constant was measured by the Q-meter method. The insulating property at high temperature was measured up to 700 °C according to JIS-2141. Microstructures of powders and sintered bodies were observed by scanning electron microscopy (SEM) and analytical electron microscopy (AEM).

3. Results and discussion

3.1. Synthesis and sintering behaviour of powder with cordierite single phase

A schematic diagram of the colloidal processing used to synthesize cordierite and cordierite–ZrO_2 composite powders is shown in Fig. 1. A drastic change of pH resulted in gelation and coprecipitation which brought about a roughly homogeneous distribution of elements in precipitated or gelated particles. Fig. 2 shows the distribution of each element in the precursor gel. Energy-dispersive spectroscopy (EDS) of the gel at various points and widening of the probe diameter at the same point indicated heterogeneity of the order of a few hundred nanometres. Each part indicated differences in atomic ratio, and this heterogeneity was not removed by widening the analysis

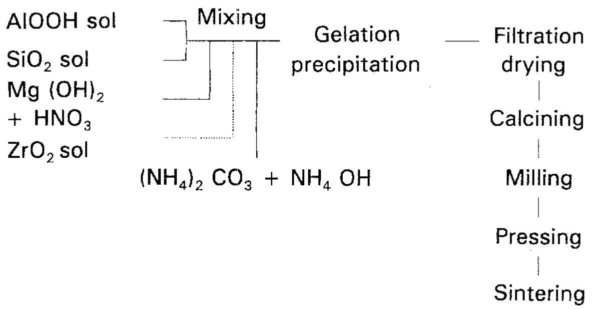

Figure 1 Schematic diagram of colloidal processing.

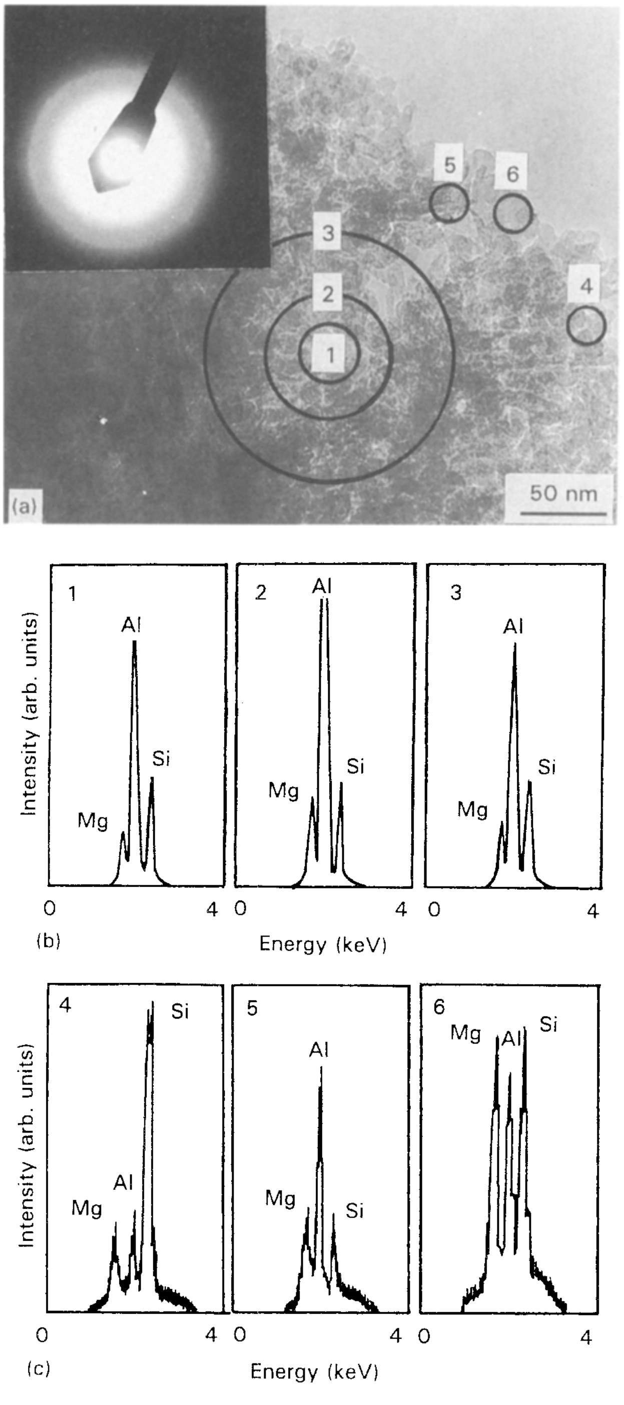

Figure 2 TEM photograph and EDS spectrum of as-dried gel.

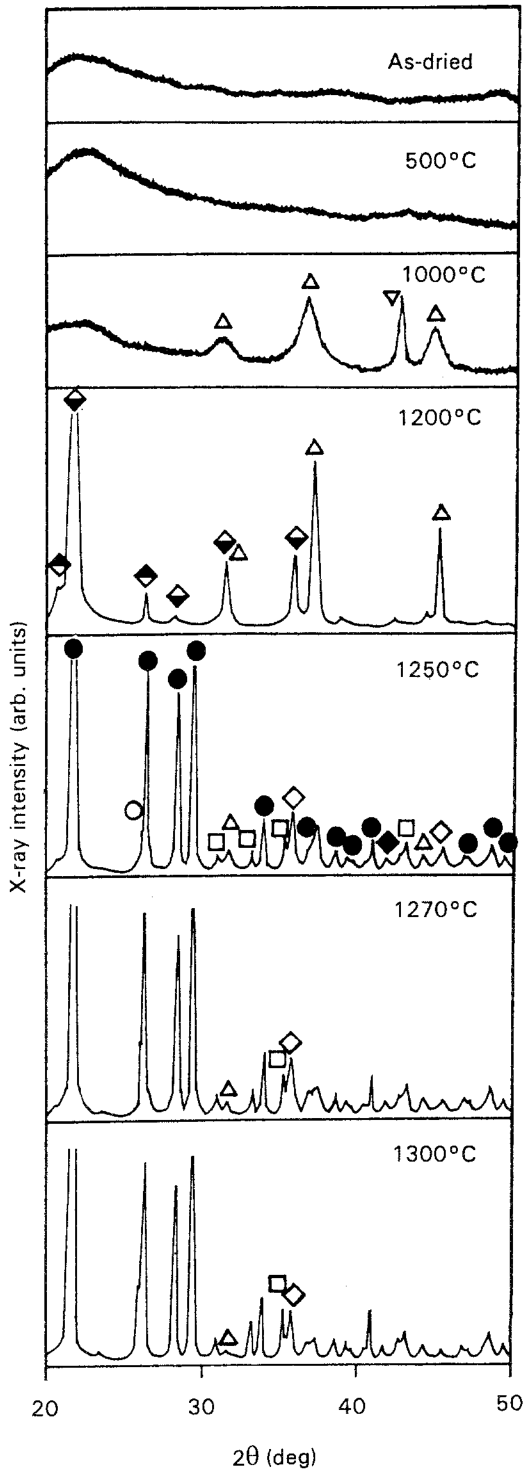

Figure 3 X-ray diffraction patterns of powders as-dried and calcined at different temperatures for 1 h. (□) Mullite, (△) spinel, (▽) periclase, (◇) sapphirine, (◆) forsterite, (⬘) cristobalite, (⬙) low quartz, (●) cordierite (α, β), (○) cordierite (μ).

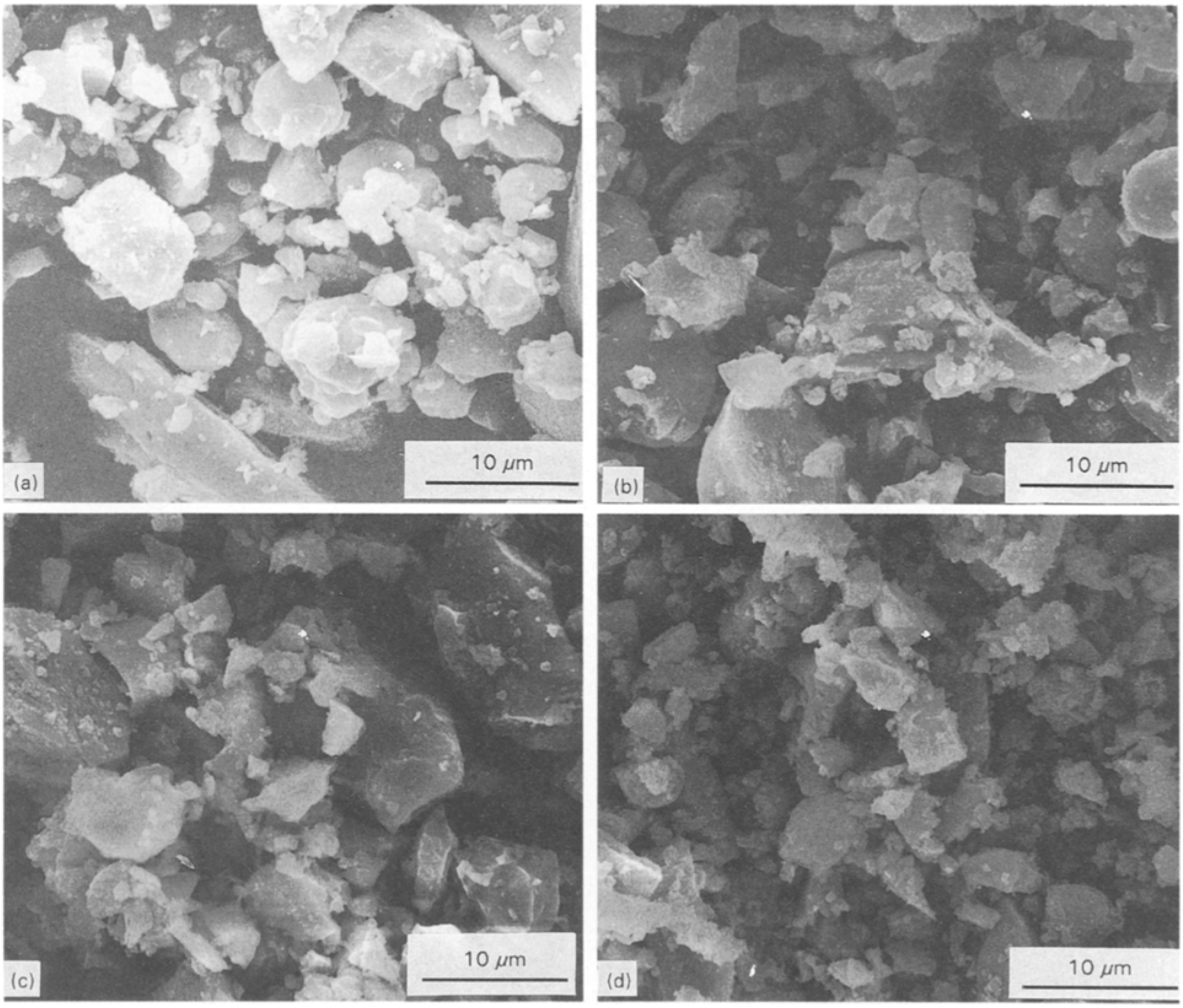

Figure 4 SEM photographs of powders calcined at (a) 1200 °C, (b) 1250 °C, (c) 1270 °C and (d) 1300 °C.

beam from 30 to 150 nm. The smallest particles were identified as SiO_2, fibrous ones as AlOOH, and platy ones as $MgCO_3$ by means of EDS micro-analysis. Electron beam micro-diffraction showed a halo pattern which indicated an amorphous nature for all parts of the gel.

The as-dried gel was amorphous during heating to 500 °C, and then spinel and periclase were crystallized. At 1200 °C, cristobalite, spinel and low quartz were mainly indentified as crystal phases. Above 1250 °C they were turned to cordierite with a small amount of mullite, spinel and sapphirine, and the crystalline phase assemblage showed no significant phase change above 1300 °C (Fig. 3).

The morphologies of powders calcined at 1200, 1250, 1270 and 1300 °C are shown in Fig. 4. There were no significant differences in the morphology of powders. These powders, with particle sizes ranging from a few micrometres to above 10 μm, were ground for 24 h to obtain submicrometre powder as the raw material for sintering.

The relationship between the calcination temperature and the bulk density and amount of water absorbed by the sintered body obtained by sintering at 1440 °C for 1 h is shown in Fig. 5. The bulk density of cordierite sometimes exceeds the theoretical density because of the formation of mullite as recrystallized from the liquid phase (the theoretical density of cordierite is 2.54 $g\,cm^{-3}$, whereas that of mullite is 3.18 $g\,cm^{-3}$). The amount of water absorption, which indicates the porosity at the surface of the sintered body, was used as the index of sinterability together with the bulk density. The water absorption value of samples sintered at 1430 °C exceeded 0.5% and above 1455 °C all sintered bodies were melted. The optimum

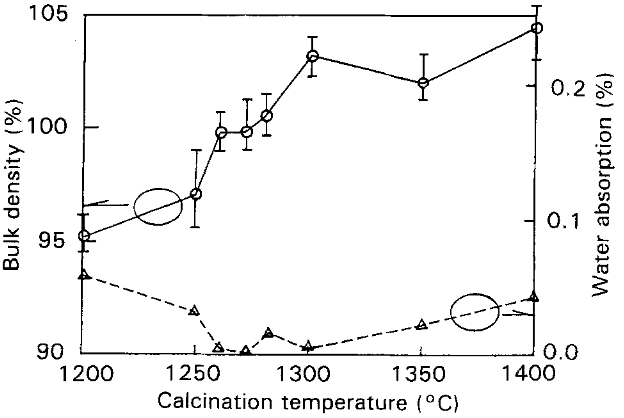

Figure 5 Relationship between calcining temperature and (○) sintered bulk density and (△) water absorption ratio of sintered body.

sintering temperature was 1440–1450 °C. Calcination temperatures ranging from 1200 to 1400 °C were examined under these sintering conditions; below 1200 °C cordierite was not synthesized and above 1300 °C synthesized cordierite grains were strongly aggregated in calcined powders, so the amount of water absorption of sintered bodies by using the powder calcined at 1250–1300 °C was close to 0%.

In multi-component systems, a heterogeneous distribution of elements in the powder sometimes pro-

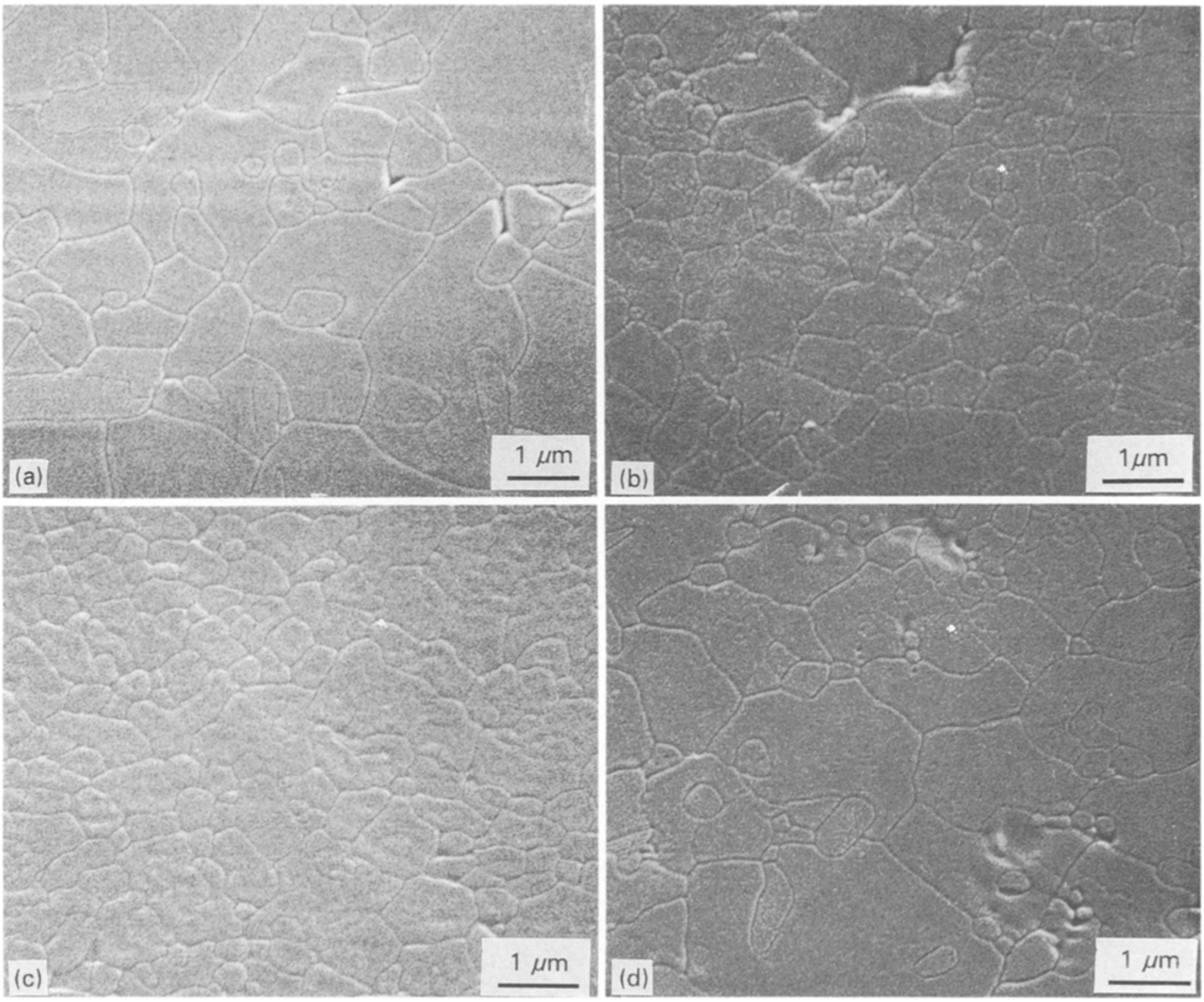

Figure 6 (a–d) SEM photographs of polished and thermally etched surfaces of sintered bodies for each calcination temperature (as in Fig. 4) and (e) X-ray diffraction pattern of body sintered at 1440 °C for 1 h.

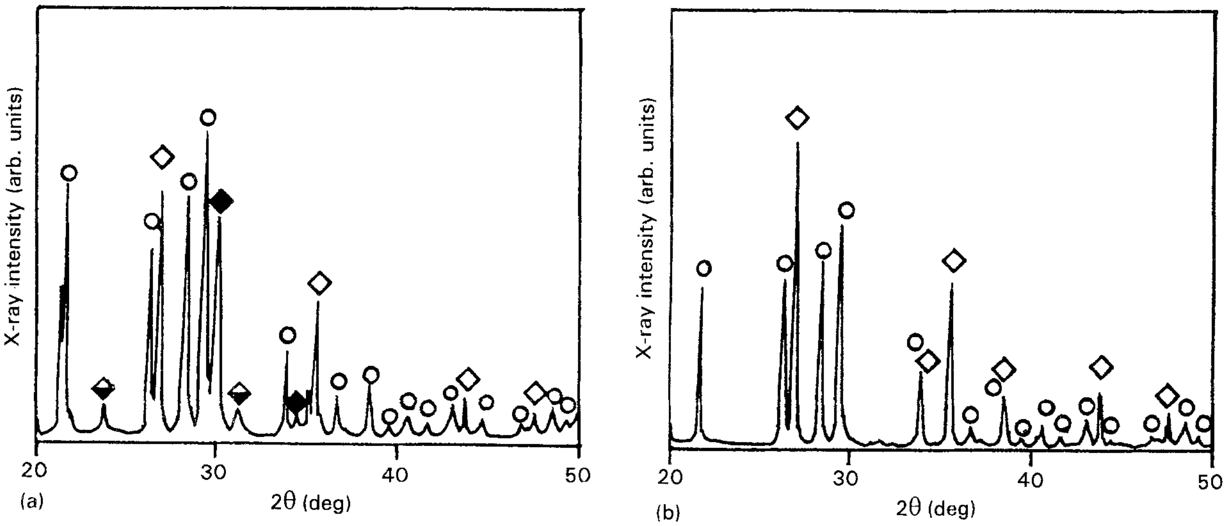

Figure 7 X-ray diffraction patterns of cordierite–15 wt % ZrO_2 composite for (a) powder calcined at 1250 °C and (b) the body sintered at 1420 °C. (○) Cordierite, (⬖) m-zirconia, (◆) t-zirconia, (◇) zircon.

motes densification with a small amount of liquid phase during the sintering [7]. This liquid phase is generated in the area corresponding to the components of lower melting temperature in the system. Fig. 5 and consideration of the results from Figs 3 and 4 suggest that the optimum calcination temperature to be followed by sintering at 1440 °C was around 1270 °C. The bulk density reached 100% of theoretical density in the same temperature range, and this indicates densification without the formation of mullite in the sintered body. This phenomenon is probably related to the phase assemblage (which means the heterogeneity) in small regions. The small amount of other phases such as spinel, sapphirine, mullite and forsterite in calcined powder suggested the fluctuation of composition which promotes liquid-phase sintering.

Fig. 6 shows the microstructure for each sintered body of a polished and thermally etched surface (etching at 1300 °C for 0.5 h). Significant grain growth of bodies sintered at 1200 °C (Fig. 6a) and 1300 °C (Fig. 6d) was observed. This grain growth was prob-

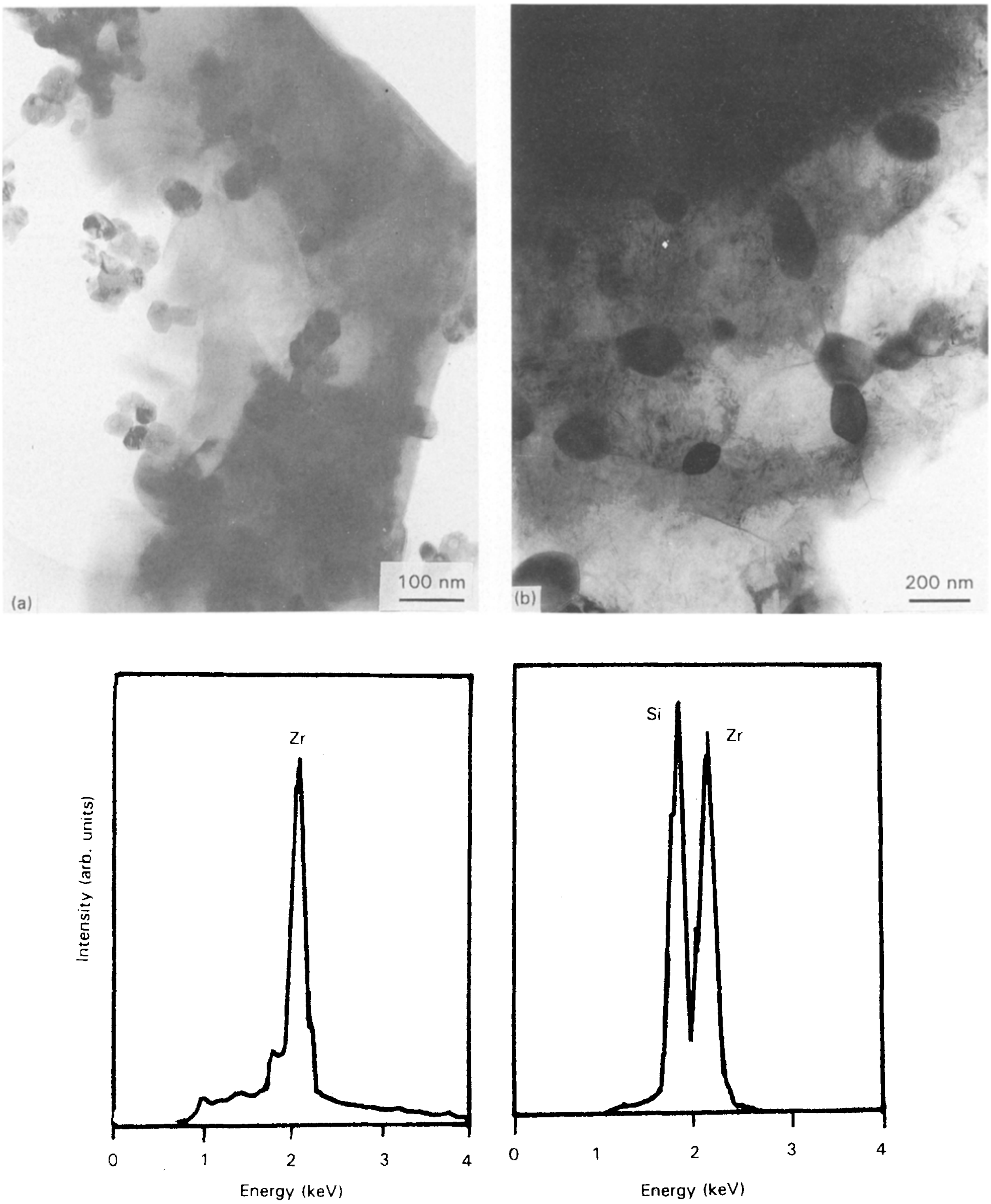

Figure 8 TEM photographs and EDS spectra for inclusions in (a) cordierite–ZrO_2 composite powder calcined at 1250 °C and (b) the sintered body obtained after treatment at 1420 °C for 1 h. ZrO_2 additive: 15 wt %.

ably related to significant heterogeneity in the powder calcined at 1200 °C and to an increased amount of mullite in the powder calcined at 1300 °C. For the body sintered at 1270 °C, the grain size was a minimum and the densely sintered body was consistent with the water absorption value of nearly 0%. X-ray diffraction of this sintered body showed a single phase of cordierite.

3.2. Synthesis and sintering behaviour of the powder of cordierite–ZrO_2 composite

ZrO_2 fine particles were introduced into the cordierite matrix by using colloidal processing. ZrO_2 sol was mixed with the sol of the cordierite component, dried and calcined at 1250 °C. Compacts of the calcined powder were sintered at 1410–1430 °C for 1 h. Calcined powder consisted of cordierite $ZrSiO_4$ and m, t-ZrO_2 with a small amount of impurity phase (Fig. 7a). TEM observation of calcined powder (Fig. 8a) shows the dispersion of ZrO_2 particles of 30–80 nm in size in the cordierite matrix.

Added ZrO_2 was turned into $ZrSiO_4$ by reaction with SiO_2 in the cordierite matrix. Fig. 7b shows the constituent phases of cordierite and $ZrSiO_4$ as the main phases in the sintered body obtained at 1420 °C. The microstructure of the sintered body showed a composite structure consisting of cordierite and $ZrSiO_4$ grains 100–200 nm in size in the cordierite matrix (Fig. 8b). $ZrSiO_4$ particles were distributed mainly in the grain boundaries of cordierite grains.

The relationship between water absorption, sintering temperature and the amount of added ZrO_2 is shown in Fig. 9. Increasing the amount of ZrO_2 additive decreased the sintering temperature. For example, the optimum sintering temperature for the powder with a ZrO_2 addition of 15 wt % was 1420–1430 °C. Above 30 wt % of additive, densification before melting was impossible. The optimum sintering temperature range was narrow in the case of ZrO_2 compared to the cordierite single phase, except for the addition of 15 wt % when it was 1420–1430 °C. This phenomenon indicates that the amount of liquid produced in sintering is increased by the addition of more ZrO_2.

3.3. Mechanical and electrical properties of cordierite and cordierite–$ZrSiO_4$ composite

The thermal expansion coefficient (TEC) of the sintered body with cordierite single phase was 1.5–1.8 $\times 10^{-6}$ °C^{-1} (RT to 1200 °C). Addition of zirconia increased the TEC monotonously (Fig. 10a). The TEC of $ZrSiO_4$ is 4.1×10^{-6} °C^{-1}. The TEC obtained for the composite was based on the sum of the coefficient of $ZrSiO_4$ in the matrix and that of the cordierite matrix. Particles of larger TEC in a matrix of lower TEC cause thermal strain (tension) and this results in the genesis of microcracks in the matrix around the particles during heating and cooling cycles. Fig. 10b shows the hysteresis of the thermal expansion curve for the first and third heating–cooling cycles. This result indicated that microcracks between the cordierite matrix and $ZrSiO_4$ particles were generated during the first cooling, which resulted in a decrease of thermal expansion.

The bending strengths of sintered bodies of cordierite single phase and cordierite–$ZrSiO_4$ composite prepared under optimum conditions were investigated by means of the three-point bending test. Fig. 11

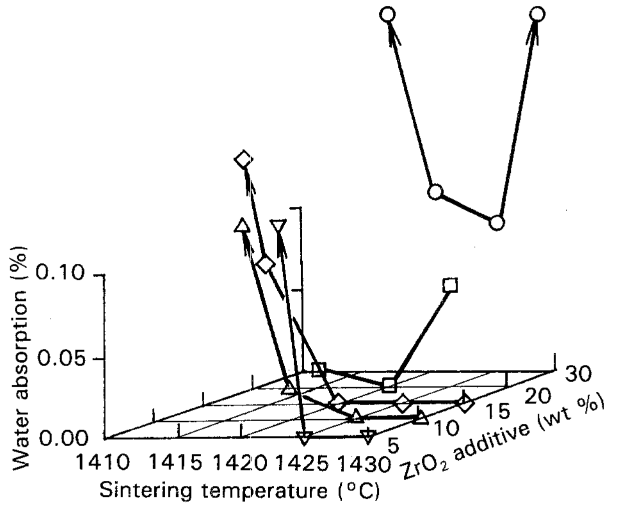

Figure 9 Relationship between water absorption of sintered body, the amount of ZrO_2 additive and the optimum sintering temperature. Additive (wt %): (▽) 5, (△) 10, (◇) 15, (□) 20, (○) 30.

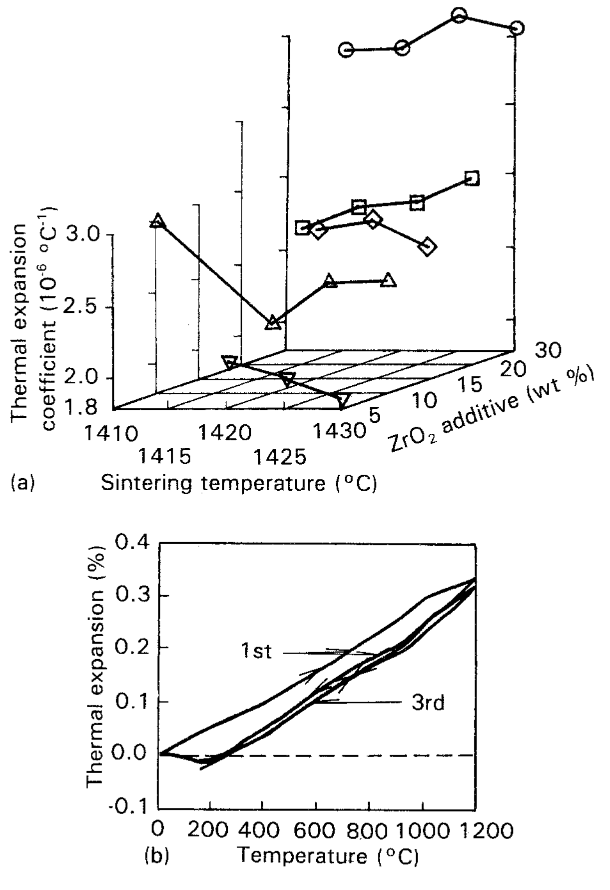

Figure 10 (a) Relationship between sintering temperature, the amount of ZrO_2 additive and the thermal expansion coefficient of cordierite–$ZrSiO_4$ composite; additive (wt %): (▽) 5, (△) 10, (◇) 15, (□) 20, (○) 30. (b) Hysteresis of thermal expansion curve for temperature cycling.

shows the increase of bending strength (σ) from less than 110 MPa (0 wt % ZrO_2) to above 140 MPa (25–30 wt %).

Cordierite is expected to have a low dielectric constant. The cordierite single phase obtained had a dielectric constant value (ε) of 2.0–4.5 and a dielectric loss ($\tan \delta$) of $2.2–10 \times 10^{-4}$. Addition of ZrO_2 effected a slightly increase in ε and $\tan \delta$ except for the case of the addition of 30 wt %; in this case the sintered body was not sufficiently densified. The insulating property was significantly affected by addition of ZrO_2. Fig. 12 shows the relationship between $\log \rho$ and $1/T$. Addition of ZrO_2 decreased the resistivity (ρ) at higher temperatures. The Te value for sintered cordierite was above 1500 °C (this value was obtained by extrapolation of the linear $\log \rho$ versus $1/T$ plot to the point $\log \rho = 6$), but it was decreased to less than 1300 °C by 30 wt % ZrO_2 addition.

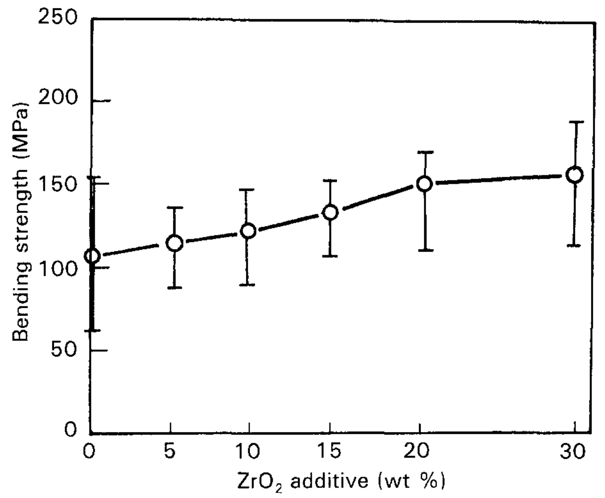

Figure 11 Bending strength of sintered body of cordierite and cordierite–$ZrSiO_4$ composite.

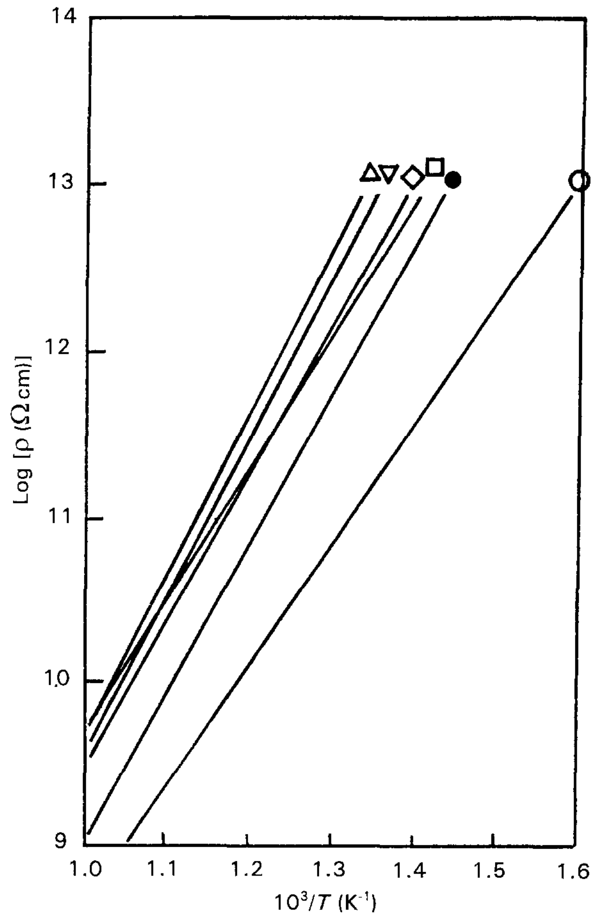

Figure 12 Relationship between the amount of ZrO_2 additive, $\log \rho$ and temperature. Additive (wt %): (●) 0, (▽) 5, (△) 10, (◇) 15, (□) 20, (○) 30.

4. Conclusions

1. A powder having a cordierite single phase and a powder having cordierite with ZrO_2 were synthesized by colloidal processing.
2. The calcination temperature affected the sinterability of the powder having a cordierite single phase. Calcination at 1270 °C followed by sintering at 1440 °C was optimum for this powder.
3. Addition of ZrO_2 decreased the optimum sintering temperature.
4. The thermal expansion coefficient of cordierite single phase, $1.5–1.8 \times 10^{-4}\,°C^{-1}$, was increased by ZrO_2 addition. The bending strength was enhanced by ZrO_2 addition whereas the electrical properties were suppressed by the additive.

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Received 6 July 1992
and accepted 27 April 1993