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# Emulsion processing as a novel route to cordierite

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Emulsion processing has been utilised to produce sub-micron spherical particle precursors, which can be sintered to form dense $\alpha$-cordierite ceramics at temperatures as low as 1100°C after 2 hours. The products are slightly magnesium deficient, resulting in trace amounts of mullite being present in the final ceramics. Flexural strengths of 73 MPa have been measured, with a Weibull modulus of 12. The Vickers hardness was measured at 8.5 GPa, and the fracture toughness at 2.2 MNm$^{-3/2}$.

## 1. Introduction

Cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) is an important structural ceramic due to its excellent resistance to chemical attack, and its high mechanical strength, even at elevated temperatures. It also exhibits high thermal shock resistance, low thermal expansivity, and is an electrical insulator with a low dielectric constant. Despite these useful characteristics, however, cordierite is particularly difficult to sinter to near-theoretical density, and pure $\alpha$-cordierite can only reach full TD (theoretical density) at temperatures approaching its melting point (1450°C) [1]. As a result, sintering from a cordierite component is preferred. Cordierite is currently the material of choice as a catalyst support for catalytic converters in the automotive industry, where each device contains approximately one kilogram of cordierite.

Cordierite has three different polymorphs, $\alpha$, $\beta$, and $\mu$, of which the $\alpha$ (hexagonal) form is the most thermodynamically stable polymorph, with a melting point around 1450°C. The $\beta$ (orthorhombic) form is also stable and transforms into the $\alpha$ phase at around 1400°C. The $\mu$ phase (distorted hexagonal) forms $\alpha$ cordierite above 1000°C. To overcome the problems of densification, hot isostatic pressing (HIP) can be employed, or sintering aids added. HIP, although a very good technique, is expensive, making the process economically unattractive, while the addition of sintering aids, although relative cheap, results in the degradation of the thermal expansivity, dielectric behaviour, and high temperature mechanical properties.

Industrially, $\alpha$-cordierite is produced by a solid state reaction, using talc, kaolin, magnesia and alumina as the starting materials. They are milled together and then extruded into a honeycomb structure suitable for catalyst support, before sintering above 1300°C to promote densification and phase transformation to $\alpha$-cordierite. The particle sizes of the starting materials play a crucial role in the properties of the final ceramic. Nakahara *et al.* [2] showed that using precursors with large particle sizes could result in the production of enstatite and mullite, resulting in an increase in the thermal expansivity and poor thermal shock resistance. The presence of any glassy phase in the final ceramic has been shown to lead to poor thermal shock resistance due to the thermal expansion mismatch between them and the $\alpha$-cordierite [3]. Flexural strengths for cordierite produced in this fashion are reported at between 20 and 75 MPa [2].

As a result of its desirable characteristics, much research has been directed towards improving the synthesis of $\alpha$-cordierite in order to produce high purity, easily densified material. Dupon *et al.* [4] reported the use of a bismuth oxide flux, which remained mostly at the grain triple points of the densified body, without significantly affecting the thermal expansivity or dielectric constant. Okuyama *et al.* [5–9] reported a coprecipitation method for the production of a cordierite precursor. These powders could be densified by firing at 1100°C for 1 hour, and with the addition of 5 wt% $\alpha$-cordierite seed particles this could be reduced to 900°C. The seeded sample exhibited a flexural strength of 190 MPa, compared to 50 MPa for the unseeded sample. Bedard and Flanigen [10] reported the synthesis of $\alpha$-cordierite by the thermal decomposition of magnesium zeolite B at 800°C to form an amorphous powder

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which could be sintered to 96% theoretical density (TD) $\alpha$-cordierite after 4 hours at 1100°C.

Sol-gel processing has been investigated by a number of different researchers. Karagedov *et al.* [11] prepared $\alpha$-cordierite by refluxing mixtures of magnesium, aluminium and TEOS (tetraethylorthosilicate) in ethylene glycol, followed by hydrolysis and gelation by the addition of water. The dried gel underwent thermolysis at 540°C. Sintered pellets of the resulting powder of 97% TD were obtained. Maeda *et al.* [12] formed $\alpha$-cordierite from a gel prepared by refluxing TEOS, aluminium iso-propoxide, and magnesium ethoxide in ethanol and diethyl glycol monomethyl ether (DEMM), the amount of which, controlled the hydrolysis rate of the aluminium and magnesium alkoxides. Pure $\alpha$-cordierite could be produced after firing at 1100°C for 2 hours. Douy *et al.* [13] proposed two different polymer-gel processes starting from combinations of TEOS, aluminium nitrate and magnesium nitrate. Gelation was achieved by forming an organic network in-situ with acrylamide for an aqueous gel, or 2-hydroxyethyl methacrylate for an alcoholic gel. After drying, the powders were calcined at 750°C for 5 hours. Both powders could be converted to $\alpha$-cordierite after calcination at 1200°C for two hours, however, the aqueous gel contained traces of spinel. Densities approaching 98% TD were achieved.

Emulsion processing has been shown to offer an excellent route to the production of ceramic powders. Its advantages lie in the atomic scale mixing of the component precursors, leading to high homogeneity in the product, and its unique ability to produce small spherical particles [14, 15]. This comes as a direct result of the emulsion droplets, which act as tiny microreactors. This latter characteristic is very important for the production of dense sintered bodies with high mechanical strength. Another advantage is the low cost of the starting materials when compared to techniques such as sol-gel.

Previous results have shown that emulsion processing is capable of producing perovskite ceramics with high homogeneity and high sintered density [16]. In the current study we have adapted this route, which utilises water in oil (w/o) emulsions, in an attempt to produce high-density sintered cordierite with a high mechanical strength, from relatively cheap precursors.

## 2. Experimental

The aqueous component of the emulsion was prepared by dissolving magnesium nitrate hexahydrate (17.548 g, Aldrich), and aluminium nitrate nonahydrate (51.3024 g, Aldrich) in 240 ml water. TEOS (35.6128 g, Aldrich) was then added and stirred for two hours in order to hydrolyse the hydrophobic $CH_3CH_2O$- groups to hydrophilic HO- groups, thus forming a homogeneous solution. The oil phase (continuous phase) was prepared by dissolving 25.5 g Span 20 (sorbitan monolaurate, 5 wt%, Lancaster) in 600 ml (480 g) kerosene.

The aqueous phase was gradually poured into the oil phase, with stirring for 30 minutes, before being sonicated using an ultrasonic probe (Vibra Cell VCX600, Sonics and Materials Inc. (USA)) in batches of 150 ml. Different sonication regimes, varying the output amplitude, the pulsing sequence, and total sonication time, were used to investigate their effect on the emulsion formation. The emulsion was then added dropwise to a hot kerosene bath (300 ml), which was held at a constant 130–140°C. The kerosene bath was held at 140°C for a further 30 minutes to ensure complete evaporation of the aqueous phase, before being allowed to cool. The purpose of this step was to rapidly remove the aqueous phase, leaving only the solid reactants dispersed in the organic phase. The solid product was then recovered by centrifugation at 2600 rpm for 20 minutes. The product was then further dried in an oven at 100°C for 12 hours before calcination at 600°C for 3 hours to remove all the organic material (as determined by thermogravimetric analysis). Emulsions were also prepared for each of the individual metal components of the precursor mixture.

Microstructural analysis was carried out using a field emission gun scanning electron microscope (FEG SEM, Hitachi S4000), and a transmission electron microscope (TEM, Jeol JEM 4000FX), equipped with an energy dispersive X-ray (EDX, Link 2000) analysis probe, and a selected area diffraction (SAD) probe. Powder X-ray diffraction (XRD, Philips pw1050) was used to determine the phase of the products. Powders were also analysed by simultaneous differential thermogravimetric analysis (TG/DTA, Stanton Redcroft STA781).

For mechanical testing purposes, sintered bars of ceramic were prepared. Green pressed bars of approximately 70 mm × 10 mm × 3.5 mm were prepared by subjecting a mixture of 9 g of calcined powder and 6 g of binder to a pressing load of 30 kN (42 MPa). The binder consisted of 1 g of polyvinylbuterate (PVB) mixed with 10 g cyclohexanone.

Before pressing, the binder/powder mixture was allowed to stand at room temperature for 5 hours to partially remove excess solvent. After pressing, the bars were dried at 50°C for 12 hours. The addition of the binder mixture was crucial to the preparation of the green bars, which otherwise showed poor cohesiveness, and crumbled easily. The binder mixture also improved the linearity of the final sintered bars, which were otherwise too curved for meaningful mechanical tests. After drying, the bars were heated to 600°C at a heating rate of 2°C/min, and held at temperature for two hours before being further heated at 2°C/min to 1100°C and held at temperature for a further two hours before cooling. The dwell at 600°C was essential for the complete burnout of the organic binder. X-ray diffraction showed that the bars consisted of $\alpha$-cordierite. The densities of both pellets and bars were measured using the Archimedes method.

For flexural strength measurements, the large faces of the sintered bars were ground flat with a 70 $\mu$m finish. One side was then further polished to 14 $\mu$m, and finally 1 $\mu$m. the final dimensions of the bars were approximately 6.3 mm × 2.2 mm × 44 mm. The flexural strength (3-point bend) was then measured using a standard Instron testing machine, attached to a PC for data logging. The span of the bottom rollers was 30 mm, and the cross-head speed was 0.5 mm/min.

The flexural strength ($\sigma$) was given by the equation, $\sigma(Nm^{-2}) = 3Ps/2\,BW^2$ (Equation 1) where $P$ is the load at fracture ($N$), $s$ is the support span length ($m$), $W$ is the width of the specimen ($m$), and $B$ is the breadth of the specimen ($m$). Visual examination of the fractured specimens showed that fracture did occur at the mid-span position. Wedging was corrected for using the equation $\sigma_w = \sigma(1 - 0.1776\ \mathrm{W/s})$ (Equation 2), where $\sigma$ is given by Equation 1 [17]. The Weibull modulus was calculated from the gradient of a plot of lnln$[1/P_s]$ vs ln($\sigma_n$), where $P_s$ is the survival probability calculated from $P_s = 1 - i/(n+1)$; $n$ is the total number of specimens; $I$ is the specimen number in order of ascending strength; and $\sigma_n$ is the 3-point flexural strength ($\sigma_w$) of the nth specimen.

A Vickers microindenter was used to measure the hardness of the specimen. The load used was 500 g or where necessary 1 kg. Before indentation, samples were coated using a gold coater to improve the reflectance of the sample [18]. The coating thickness was approximately 20 nm, allowing the indentations and cracks to be seen more clearly. The Vickers hardness ($H_v$) was calculated as $H_v$ $(Nm^{-2}) = 1.8544P/d^2$ (Equation 3), and the fracture toughness ($K_c$) calculated as $K_c$ $(Nm^{-2}) = 0.0824P/C^{3/2}$ (Equation 4) [19]. In this case, $P$ is the load for indentation ($N$), $d$ is the diagonal length of the indentation ($m$), and $C$ is the crack length extending from the centre of the indentation ($m$).

## 3. Results and discussion

As can be seen from the XRD traces in Fig. 1, neither the as-produced powder, nor the powder which has been calcined at 600°C for 3 hours, is crystalline, but instead, the precursors have mixed together to form amorphous particles. The FEG SEM micrograph in Fig. 2, and the TEM micrograph in Fig. 3, show typical morphologies for the unfired particles after emulsion processing. The spherical morphology is evident, but from Fig. 3, it is clear that the 100 nm spheres are made up from far smaller primary particles approximately 5–10 nm in diameter. This type of morphology has been observed in other systems where emulsions have been used to prepare ceramic powders, and the spheres have been shown to be hollow [16, 20]. It has been proposed that as the emulsion is dropped into the hot kerosene bath, the water rapidly expands as it evaporates, carrying the precursors to the outer edges of the droplets. As the gaseous phase is formed, the precursors precipitate in the shape of the droplet, thus giving a hollow sphere. The holes between the primary particles are the inevitable consequence of the water in the sphere centres escaping as it evaporates [16]. The large spheres come as a direct result of the size of the aqueous droplets in the emulsion, and so can be controlled by controlling the droplet size by varying the surfactant concentration. The SAD pattern shown in Fig. 4 confirms the

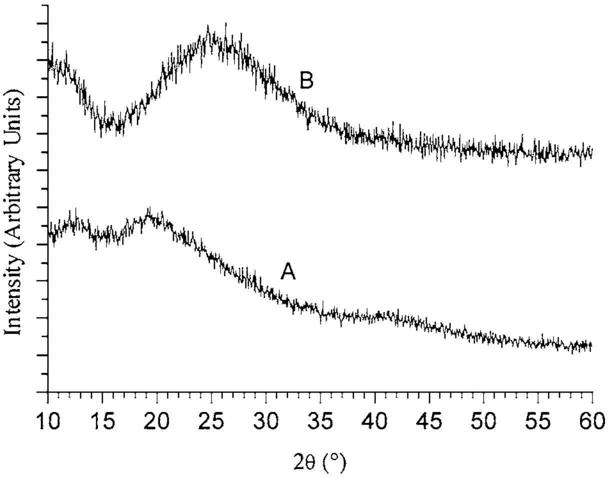


*Figure 1* XRD spectra for emulsion-derived powders. A) as-produced powder; and B) powder calcined at 600°C for 3 hours.

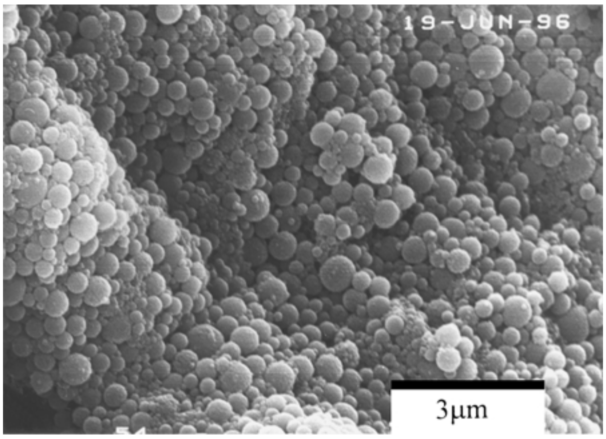


*Figure 2* FEG SEM micrograph showing the spherical morphology of the as-produced emulsion powders.

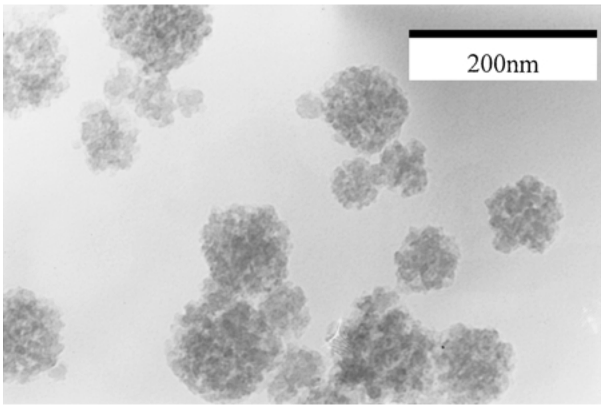


*Figure 3* TEM micrograph showing the primary particles which make up the spherical emulsion powder particles.

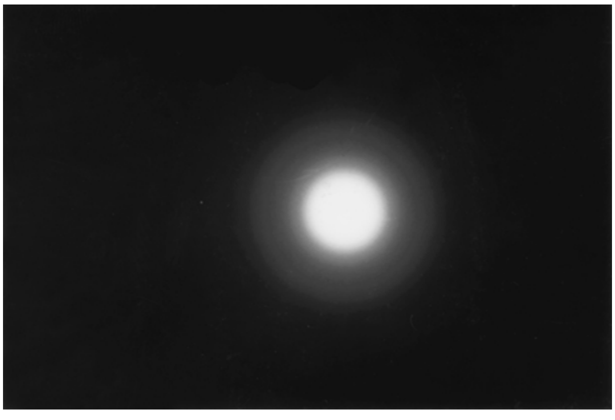


*Figure 4* TEM SAD pattern showing the amorphous nature of the as-synthesised powder particles.

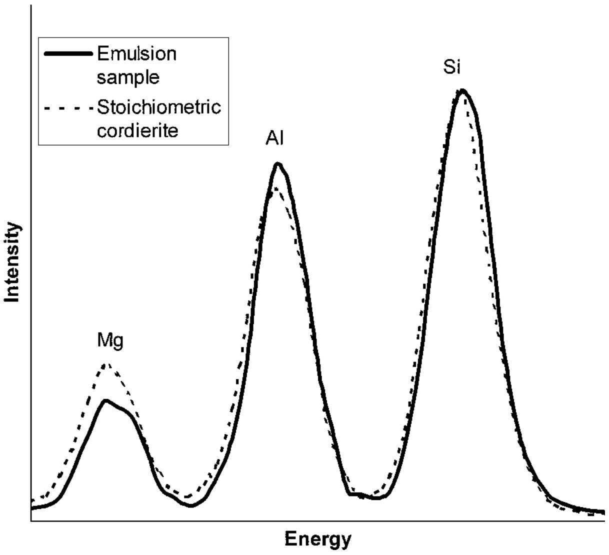


*Figure 5* TEM EDX showing the magnesium deficiency of the emulsion-derived powder compared to stoichiometric powder.

amorphous state of the powder particles, proving that they are not microcrystalline.

TEM EDX showed that the distribution of aluminium, magnesium and silicon was homogeneous, both within the particles, and across the whole particle population, proving that atomic mixing did in fact occur in the emulsion. Thus the rapid dehydration of the emulsion processing removed the problems associated with the different precipitation rates in solution. Fig. 5 shows a typical EDX trace for the emulsion particles. It should also be noted that the emulsion produced powders were uniformly magnesium deficient, when compared to stoichiometric cordierite obtained from Baikowski Chemie. This is attributed to the partial melting of the magnesium nitrate component of the emulsion (melting point 89°C). Magnesium nitrate does not decompose readily, even at 140°C, unlike the aluminium nitrate and TEOS, and so a small amount is lost as a molten liquid to the kerosene bath, where it deposits on the side of the vessel. This leaves the product spheres slightly deficient in magnesium.

The XRD spectra in Fig. 6 show the phase transformations, as the calcined powder is sintered at high temperature. As expected [21, 22], for a near stoichiometric mixture, initially at 900°C $\mu$-cordierite is formed, however, as the calcination temperature reaches 1000°C, $\alpha$-cordierite has become the predominant phase, together with trace quantities of $\mu$-cordierite and mullite $(3Al_2O_3 \cdot 2SiO_2)$. Above 1100°C, all the $\mu$-cordierite has been eliminated, and only the $\alpha$-cordierite, and traces of mullite remain. The presence of the mullite phase can be explained by the magnesium deficiency in the precursor powder. In all cases, the calcination temperature was reached by a ramp rate of 2°C/min, and the temperature was held for 2 hours. The DTA trace shown in Fig. 7 exhibits exotherms at 1020°C and 1055°C, which can be attributed to the crystallisation of $\mu$-cordierite and $\alpha$-cordierite respectively. This is typical for a homogeneous glass or powder precursor for cordierite, and further confirms the homogeneity of the precursor powder [9, 10, 21, 23].

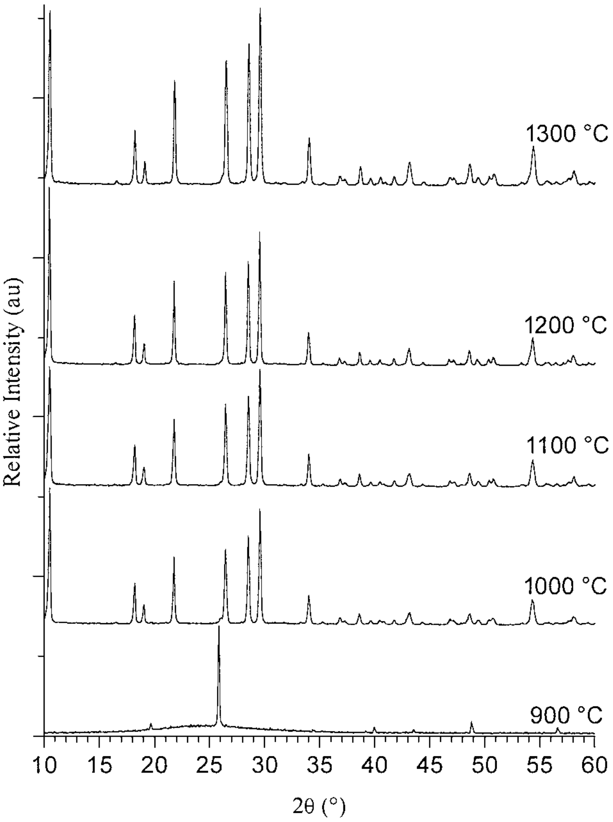


*Figure 6* XRD spectra for the calcined emulsion derived powder showing phase evolution as a function of sintering temperature.

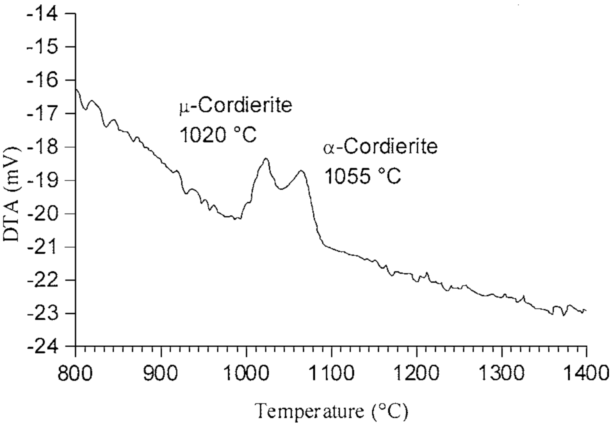


*Figure 7* DTA trace for the calcined emulsion-derived powder showing the 2 exotherms corresponding to the crystallisation of $\mu$-cordierite and $\alpha$-cordierite respectively. The heating rate was 10°C/min.

The densities of the sintered bars were shown to be between 101 and 102% TD. This rather high density can be explained by the presence of the trace quantities of mullite, which has a theoretical density of 3.17 g cm$^{-3}$ compared to 2.51 g cm$^{-3}$ for $\alpha$-cordierite. Analysis of the fracture surfaces of the samples indicated a dense microstructure with very little porosity (Fig. 8). The FEG SEM micrographs in Fig. 9 show polished and chemically etched samples of the sintered bodies. Fig. 9a reveals a cellular/dendritic type structure to the grains after etching in a solution of 0.1 wt% HF, and 0.25 wt% HCl for 20 seconds. Further etching in 10 wt% HF revealed further grain features, as the surrounding glassy phase was removed. Fig. 9b shows hexagonal platelets, identified as cordierite crystallites,

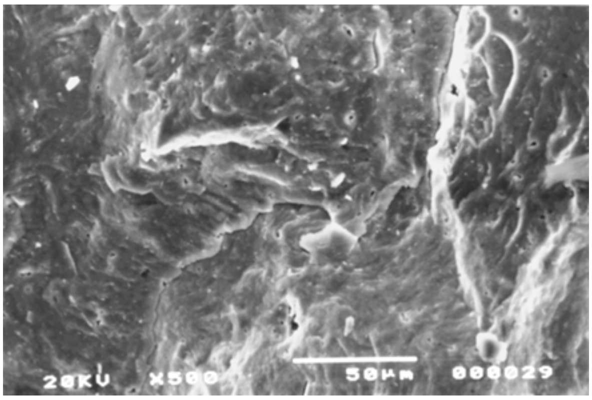
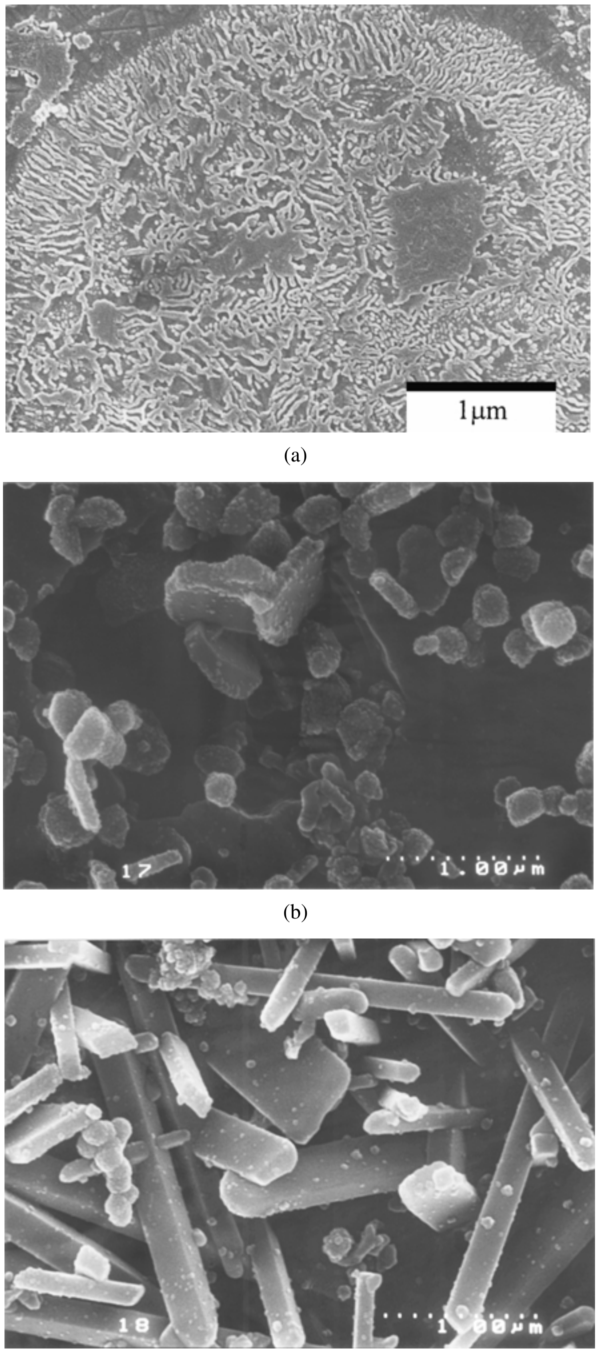


*Figure 8* SEM micrograph showing the fracture surface of a sintered bar of emulsion derived powder. The bar was sintered at 1100°C for 2 hours.



(a)

(b)

(c)

*Figure 9* FEG SEM micrographs of sintered emulsion derived powder. The powder was sintered at 1100°C for two hours and then chemically etched. a) 0.1 wt% HF, 0.25 wt% HCl, 30 s; b) 10 wt% HF, 20 s; and c) 10 wt% HF, 20 s.

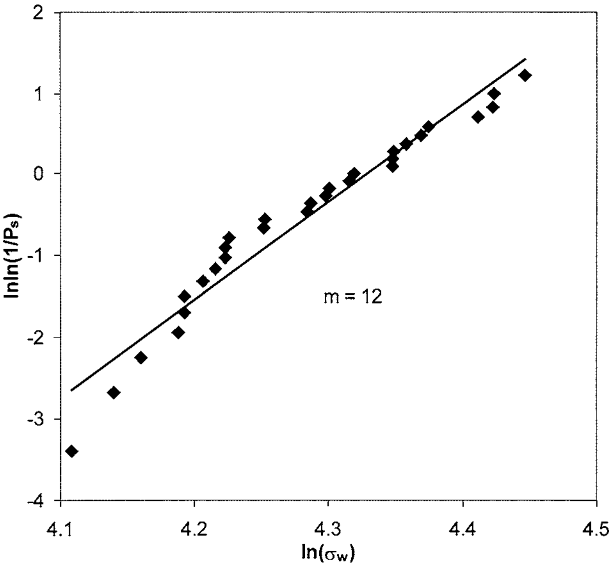


*Figure 10* Weibull plot for test bars produced from emulsion-derived powders.

while in Fig. 9c, the needle shaped crystallites of the trace amounts of mullite can be observed. Densification was probably due to the viscous flow of the large amount of glassy material in the ceramic.

The Weibull plot for the flexural strength measurements is shown in Fig. 10, and gives a Weibull modulus of 12, from a set of 29 bars. The average flexural strength was calculated to be 73 MPa, which is comparable to the best strengths produced by the industrial solid-state method [2], and significantly better than the unseeded sol-gel samples of Okuyama *et al.* [5–8]. Awano *et al.* [1] have obtained values in the range 60–150 MPa, and Moyer *et al.* [24] report strengths in the range 105–130 MPa, however, these values are for powders sintered in excess of 1420°C. As with the work of Okuyama *et al.* [9], it may be possible to significantly improve the flexural strength, if seeding is used before the precipitation phase, as this may reduce the stresses which occur during the phase transformation from $\mu$-cordierite to $\alpha$-cordierite.

The Vickers hardness value for the emulsion-produced cordierite was 8.5 GPa, which is typical for cordierite ceramics [10, 25]. The Vickers indentation fracture toughness (calculated from 21 indentations) was 2.2 $\mathrm{MNm}^{-3/2}$, which is in good agreement with the values obtained by Suzuki *et al.* [26].

## 4. Conclusions

Emulsion processing has been shown to be a viable method for producing $\alpha$-cordierite with good mechanical properties from cheap precursor materials. $\alpha$-cordierite of theoretical density can be achieved at a sintering temperature of 1100°C after 2 hours. The material has been shown to be slightly magnesium deficient, due to the low melting point of the magnesium nitrate starting material. This resulted in the formation of small amounts of mullite in the final ceramic material. The flexural strength of the material has been measured at 73 MPa, with a Weibull modulus of 12. The Vickers hardness was measured at 8.5 GPa, with a fracture toughness of 2.2 $\mathrm{MNm}^{-3/2}$. The ceramic was shown to have a considerable amount of glassy material after sintering, which contributed to the high densities achieved.

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