

# Organic Gels in the Preparation of Silico-aluminate Powders. II. Cordierite

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## Abstract

The elaboration of cordierite powders from aqueous or alcoholic solutions, gelled by organic polymers, has been studied. The aqueous solution, made from Al and Mg nitrates or citrates and Si alkoxide, tetraethylorthosilicate (TEOS) or 3-(triethoxysilyl)propylamine (TESPA), is gelled by polyacrylamide and the aqueous gel is calcined at 750°C. The behaviour of the powder depends strongly on the precursor solution. A powder produced from citrates and TESPA expands upon sintering to a porous cordierite, while that elaborated from nitrates and TEOS densifies completely before crystallizing into  $\mu$ - and then  $\alpha$ -cordierite.

In the same way, an ethanolic solution of nitrates and TEOS, gelled by poly(2-hydroxyethyl methacrylate) (pHEMA) produces a very homogeneous powder that densifies completely;  $\alpha$ -cordierite is obtained at a particularly low temperature (1000°C).

Die Herstellung von Cordieritpulvern aus wässrigen oder alkoholischen Lösungen, die durch Zugabe organischer Polymere gelierten, wurde untersucht. Wässrige Lösungen, die aus Al- und Mg-Nitraten oder -Zitrat und Si-Alkoxid, TEOS oder 3-(Triethoxysilyl)propylamin (TESPA) hergestellt wurden, wurden mit Polyacrylamid geliert. Dieses wässrige Gel wurde bei 750°C kalziniert. Das Verhalten der Pulver hängt in großem Maße von der verwendeten Ausgangslösung ab. Pulver, die aus Zitrat und TESPA gewonnen wurden, dehnten sich beim Sintern aus und bildeten porösen Cordierit. Jene aus Nitrat und TEOS verdichteten völlig, ehe sie zu  $\mu$ - und anschließend zu  $\alpha$ -Cordierit kristallisierten. In analoger Weise ergab eine Lösung aus Nitraten und TEOS in Äthanol, die mit Poly(2-hydroxyäthyl methacrylat) (pHEMA) geliert wurde, ein sehr

homogenes Pulver das völlig verdichtete. Bereits bei sehr niedrigen Temperaturen (1000°C) bildete sich  $\alpha$ -Cordierit.

L'élaboration de poudres de cordiérite par voie de solutions aqueuses ou alcooliques, gélifiées par des polymères organiques, a été étudiée. Les solutions aqueuses sont réalisées à partir de nitrates ou citrates d'Al et Mg et d'un alcoxyde de Si, TEOS ou triéthoxysilyl-3-propylamine (TESPA), puis gélifiées par le polyacrylamide. Les gels aqueux sont ensuite calcinés à 750°C. Le comportement de la poudre dépend fortement de la nature de la solution précurseur. Alors qu'une poudre obtenue à partir de citrates et TESPA gonfle pour former une cordiérite alvéolaire, très peu dense, celle élaborée à partir de nitrates et TEOS densifie complètement avant de cristalliser en cordiérites  $\mu$  puis  $\alpha$ .

De la même manière, une solution éthanolique de nitrates et TEOS, gélifiée par le polyméthacrylate d'hydroxy-2-éthyle (pHEMA), produit une poudre très homogène qui densifie complètement, et la cordiérite  $\alpha$  est obtenue à plus basse température (dès 1000°C).

## 1 Introduction

Owing to their lower dielectric constant and thermal expansion coefficient than alumina or mullite, cordierite and cordierite-based glass-ceramics are promising materials for electronic packaging.<sup>1,2</sup> However, cordierite ceramics are difficult to sinter without aids<sup>2</sup> when elaborated by the solid-state reaction of oxides mixture. If the sintering of melt-quenched glass powder begins at low temperature, around 900°C, crystallization occurs rapidly and unfortunately halts this shrinkage, so hot pressing is

necessary for the complete densification below 1000°C.<sup>3</sup>

Recent progress in processing chemistry has enabled the preparation of pure and amorphous cordierite powders which sinter at low temperature, below 1000°C, before crystallization occurs.<sup>4</sup> The amorphous powder transforms first to a meta-stable phase,  $\mu$ -cordierite, and, upon further heating, to the stable phase,  $\alpha$ -cordierite. In contrast, in the solid-state reaction  $\mu$ -cordierite is not formed; instead the first crystallized phase is spinel,  $\text{MgAl}_2\text{O}_4$ , while  $\alpha$ -cordierite is obtained only at much higher temperature by reaction of spinel with silica.

Homogeneous powders are only obtained by sol-gel methods. Cordierite, i.e.  $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ , is a ternary silico-aluminate oxide. While mullite, i.e.  $2\text{SiO}_2 \cdot 3\text{Al}_2\text{O}_3$ , a binary oxide, has been obtained by a great number of sol-gel preparations, from alcoholic or aqueous solutions,<sup>5</sup> the elaboration of cordierite is more problematic, and low-temperature sinterable powders have been prepared only from alcoholic solutions. Metal alkoxides solutions have been used<sup>4,6-8</sup> but a high degree of homogeneity is difficult to achieve because of differences in the hydrolysis rates of the alkoxides. Tetraethylorthosilicate, the silicon alkoxide, may be partially hydrolysed prior to being mixed with the other alkoxides. In other preparations, the Mg alkoxide has been made from Mg powder<sup>9</sup> or replaced by Mg nitrate,<sup>10</sup> acetate<sup>11-13</sup> or chloride,<sup>14</sup> sometimes in association with a chelated Al alkoxide.<sup>13,14</sup> Al and Mg nitrates have also been used to replace the respective alkoxides.<sup>12</sup> Cordierite fibers have been made from alcoholic solution of ethyl silicate, an Al organometallic complex, the 'aluminium chlor-hydrox', and Mg chloride.<sup>15</sup> Mullite cordierite composites powders have been prepared by an aqueous sol-gel method, from silica and boehmite sols and Mg nitrate<sup>16</sup> but no low-temperature sinterable cordierite has been reported.

Recently, a new process has been described, where the chemical homogeneity of multiple oxides is improved by gelling precursor aqueous solutions by an independent organic polymeric network, using polyacrylamide gel;<sup>17</sup> Part I of this article<sup>18</sup> is devoted to the preparation of pure and fine mullite powders by this process, from aqueous or organic solutions. Powders which crystallize completely to mullite at 970°C have been obtained. The present paper concerns the elaboration of cordierite powders by this process, from aqueous solutions with polyacrylamide gel, and from alcoholic solutions with poly(2-hydroxyethyl methacrylate) (pHEMA).

## 2 Experimental

### 2.1 Chemicals

Aluminium nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 98.5%, Merck) and magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 98%, Carlo Erba) are the sources of aluminium and magnesium, respectively. Tetraethylorthosilicate (TEOS;  $\text{Si}(\text{OC}_2\text{H}_5)_4$ , 98%, Merck) and 3-(triethoxysilyl)propylamine (TESPA;  $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$ , 99%, Merck) are sources of silicon. Acrylamide, *N,N'*-methylene diacrylamide and 2-hydroxyethyl methacrylate (Merck) are the monomers used as-received for the organic gelation of the solutions.  $\alpha, \alpha'$ -Azobisisobutyronitrile (AIBN; Fluka) is used as radical polymerization initiator.

### 2.2 Elaboration of the powders

#### 2.2.1 Aqueous route

The aqueous solutions are first made by dissolving the Al and Mg salts in water. The citrates solution is made by adding citric acid to the nitrates solution (one equivalent of citric acid per nitrate ion) and then ammonia to adjust the pH to the same level (pH 2.3) as for the nitrates solution. The Si alkoxide, TEOS or TESPA, is then added under vigorous stirring, at a concentration of 0.25–0.4 mol litre<sup>-1</sup>. A clear aqueous solution is obtained.

In 100 ml of the clear fresh aqueous solution containing Al, Mg and Si in the stoichiometric ratios 6 g of acrylamide and 0.8 g of *N,N'*-methylene diacrylamide are first dissolved. The solution is heated over a boiling water bath with magnetic stirring and, as soon as the temperature reaches 80°C, AIBN (0.1 g), previously dissolved in hot ethanol (1 ml), is introduced; gelation occurs in 1 to 2 min.

Solutions made from nitrates and TEOS have also been gelled at room temperature, without addition of AIBN, by degassing under the vacuum of a water pump. In this case the gelation needs longer time and occurs after a few tens of minutes or even a few hours. The aqueous gels are treated in a microwave oven in order to obtain rapidly a dry residue that is then calcined at 2°C min<sup>-1</sup> to 750°C and maintained at this temperature for 5 h.

#### 2.2.2 Alcoholic route

The alcoholic solution is made by dissolving Al and Mg nitrates and TEOS in ethanol (96%). In 100 ml of this solution 2-hydroxyethyl methacrylate (10 g) and *N,N'*-methylene diacrylamide (2g) are added and the solution is refluxed over a water bath. AIBN (0.1 g) is then added and the gelation occurs after about 15–30 min. The alcoholic gel is stored at 100°C for

15 h, slightly ground and calcined to 750°C as for the aqueous route preparation.

### 2.3 Characterization of the powders

The crystalline structures were determined by X-ray diffraction (XRD) on a Philips diffractometer using Cu K- $\alpha$  radiation. Differential scanning calorimetry (DSC) was performed at 10°C min<sup>-1</sup> with a high-temperature Setaram apparatus. The specific surface areas were measured in a Micromeritics Flowsorb II 2300 instrument by the BET method using nitrogen gas. The shrinkage of the powders, isostatically pressed at 200 MPa, was studied with a high-temperature Setaram dilatometer.

## 3 Results and Discussion

### 3.1 Aqueous solutions

#### 3.1.1 Powders elaboration

First, as for mullite powders,<sup>18</sup> various associations of Al and Mg salts/Si alkoxide were used as precursor aqueous solutions. The silicon was introduced as TEOS or TESPAs into the solution of Al and Mg nitrates or citrates. These solutions, being acid, catalysed the hydrolysis of the Si alkoxides into monomeric or oligomeric silanols and clear aqueous solutions were easily obtained. TESPAs, being a modification of TEOS by substitution of one ethoxy radical by an aminopropyl, is more water soluble and thus more rapidly hydrolysed.

The aqueous precursor solution was then gelled by in-situ formation of an organic polymeric network, the polyacrylamide gel.<sup>19</sup> The radical polymerization is favoured by AIBN addition and temperature (80°C), but in the case of nitrates-TEOS precursors the organic gelation was also obtained at room temperature without radical polymerization initiator addition, by simply degassing the solution. The gels were then rapidly reduced to dry residues in a microwave oven, and calcined to 750°C for 5 h. Table 1 lists some characteristics of the different powders.

After calcination at 750°C, light powders were

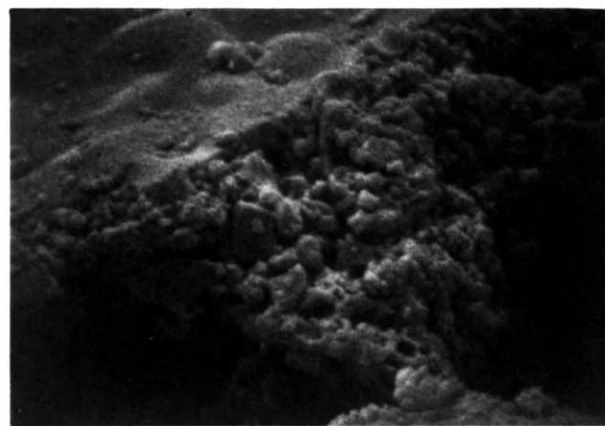


Fig. 1. Scanning electron micrograph showing the microstructure of the N1 powder (nitrates-TEOS).

obtained. They are more or less coloured and only N1 (nitrates-TEOS) is white; Fig. 1 is an SEM picture of this powder. The grains, of about 0.1  $\mu\text{m}$  size, are agglomerated in thin platelets. The specific surface area is high for the powders N1 (nitrates-TEOS) and Ci1 (citrates-TEOS), reduced for Ci2 (citrates-TESPA) and especially for N2 (nitrates-TESPA) that is, however, of very low density.

#### 3.1.2 Structural evolution versus temperature

The structural evolution of the powders versus temperature has been studied by differential scanning calorimetry and X-ray diffraction.

**3.1.2.1 Nitrates-TEOS powder.** Figure 2 shows the DSC curve obtained from the N1 powder (nitrates-TEOS) at 10°C min<sup>-1</sup>. Firstly, there is a weak endothermic peak at 831°C attributed to the vitreous transition temperature  $T_g$  of the powder. This  $T_g$  has been found to occur at the same temperature as that of melt-produced glasses of the same composition.<sup>9,10</sup> Secondly, this endothermic peak is followed by a weak exothermic peak at 862°C. X-ray diffraction was not able to precisely determine the nature of the transformation associated to this peak, the XRD diagram remaining characteristic of an amorphous powder.

Table 1. Powders elaborated by the aqueous route, calcined at 750°C (5 h) and some of their characteristics

Powder	Al and Mg salts	Si alkoxide	Colour	Specific surface area ( $\text{m}^2 \text{g}^{-1}$ )	Densification behaviour
N1	Nitrates	TEOS	White	255	Complete
N2	Nitrates	TESPA	Cream	14	Moderate
Ci1	Citrates	TEOS	Cream	235	Moderate
Ci2	Citrates	TESPA	Brown	80	Expands

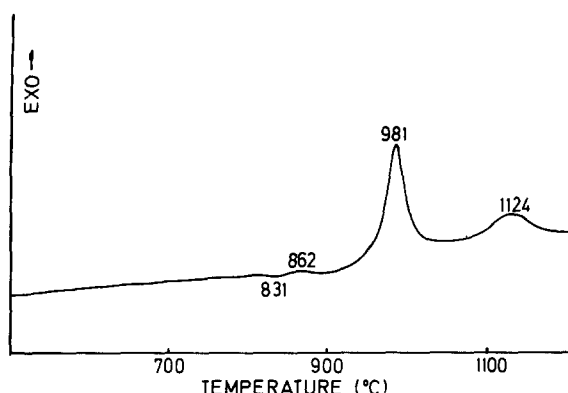


Fig. 2. DSC curve of the N1 powder (nitrates-TEOS); heating rate:  $10^{\circ}\text{C min}^{-1}$ .

The exothermic peak at  $981^{\circ}\text{C}$  corresponds to the crystallization of the  $\mu$ -cordierite, a  $\beta$ -quartz-type solid solution, and the exotherm at  $1124^{\circ}\text{C}$  corresponds to the transformation of  $\mu$ -cordierite into  $\alpha$ -cordierite, the stable structure.

Figure 3 shows the XRD diagrams of the N1 powder after annealing for 2 h at  $950^{\circ}\text{C}$  and after calcining to  $1200^{\circ}\text{C}$  at  $10^{\circ}\text{C min}^{-1}$ . At  $950^{\circ}\text{C}$  (2 h) the diagram is essentially that of  $\mu$ -cordierite, but  $\alpha$ -cordierite has begun to crystallize. There is also a little  $\text{MgAl}_2\text{O}_4$  spinel detected by the  $2\theta = 31.3, 36.9$  and  $44.9^{\circ}$  peaks. At  $1200^{\circ}\text{C}$  all the  $\mu$ -cordierite is converted into  $\alpha$ -cordierite. However, a small quantity of  $\text{MgAl}_2\text{O}_4$  spinel is still present.

Many powder preparations have been made from nitrates and TEOS and the formation of a little spinel has never been avoided. It must also be noted that, as for the mullite powders elaboration, the structural evolution and the resulting characteristics of the powders depend strongly upon the preparation conditions. The best results are obtained when the clear aqueous solution is gelled at room temperature and rapidly transformed to a dry residue in a microwave oven. When the Si alkoxide is

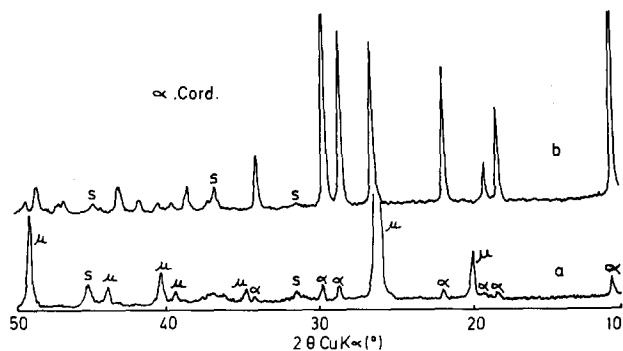


Fig. 3. XRD diagrams of the N1 powder (nitrates-TEOS): a, after 2 h annealing at  $950^{\circ}\text{C}$ , principal phase:  $\mu$ -cordierite; b, after heating up to  $1200^{\circ}\text{C}$ , heating rate:  $10^{\circ}\text{C min}^{-1}$ ;  $\alpha$ -cordierite;  $\alpha = \alpha$ -cordierite;  $\mu = \mu$ -cordierite; S =  $\text{MgAl}_2\text{O}_4$  spinel.

hydrolysed in a great excess of water, monomeric or oligomeric silanols are first obtained, which further condense and polymerize to silica gel, the kinetics of this evolution depending on concentration, temperature and pH. By reducing the duration of the transitory step of hot aqueous solution, where the formation of silica colloids is accelerated, the extent of the condensation will be restricted and more homogeneous powders will be produced.

**3.1.2.2 Other powders.** For the other powders the structural evolution versus temperature is more complicated, thermal events on the DTA curves are less marked, and the crystalline phases less pure.

After 2 h annealing at  $950^{\circ}\text{C}$ , the principal phase is  $\mu$ -cordierite with more or less important amounts of  $\text{MgAl}_2\text{O}_4$  spinel. At higher temperatures, crystallization of  $\alpha$ -cordierite is retarded and the composition of the  $\beta$ -quartz-type solid solution is modified and an additional quantity of spinel precipitates, according to the results of Schreyer & Schairer<sup>20</sup> on the recrystallization of  $\text{SiO}_2\text{-MgAl}_2\text{O}_4$  glasses. The maximum amount of spinel phase is obtained for the powders Ci1 (citrate-TEOS) and particularly N2 (nitrates-TESPA) from which  $\alpha$ -cordierite appears only beyond  $1200^{\circ}\text{C}$  at a heating rate of  $10^{\circ}\text{C min}^{-1}$ . For these two powders, at  $1380^{\circ}\text{C}$ , in addition to  $\alpha$ -cordierite, spinel and small amounts of residual  $\beta$ -quartz-type solid solution and another unidentified phase persist.

For the Ci2 powder (citrate-TESPA) the  $\alpha$ -cordierite begins to crystallize much earlier. At  $950^{\circ}\text{C}$  (2 h) there is already a little present, but this crystallization is spread over a range of temperatures and is associated with a transient increase of spinel and an unknown secondary phase. The presence of mullite as a transitory phase must also be noted. Knowing that Al citrate and TESPAs produce a powder that crystallizes completely into orthorhombic mullite at  $970^{\circ}\text{C}$ ,<sup>18</sup> it is not surprising to find the presence of mullite in the Ci2 powder. After annealing for 2 h at  $1250^{\circ}\text{C}$ , the mullite has disappeared and only traces of spinel and the unidentified phase in addition to  $\alpha$ -cordierite remain.

### 3.1.3 Dilatometric study

The more spectacular differences between the powders elaborated through the aqueous route are in their dilatometric behaviours. Samples of each powder have been isostatically pressed at 200 MPa without previous deagglomeration and heated at a constant rate of  $5^{\circ}\text{C min}^{-1}$ .

Figure 4 represents the linear shrinkage of sample

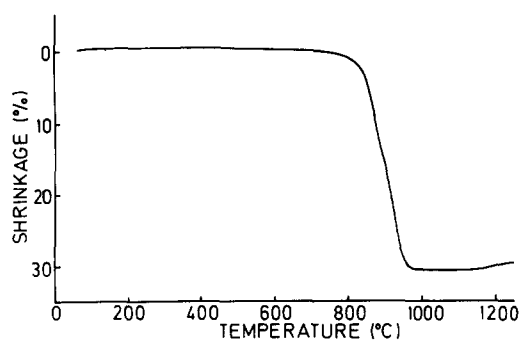


Fig. 4. Linear shrinkage of a N1 powder compact (nitrates-TEOS); heating rate  $5^{\circ}\text{C min}^{-1}$ .

N1 (nitrates-TEOS) versus temperature. It densifies between 840 and  $975^{\circ}\text{C}$  and slightly expands between 1150 and  $1250^{\circ}\text{C}$ . This weak dilatation may occur with transformation of cordierite from the  $\mu$ - to the  $\alpha$ -polymorph with a change of density (theoretical densities:  $2.587$  and  $2.512\text{ g cm}^{-3}$  for  $\mu$  and  $\alpha$  respectively). A density of  $2.62\text{ g cm}^{-3}$  has been measured for a sample annealed for 2 h at  $950^{\circ}\text{C}$ . This value is greater than the theoretical one for pure cordierite but compatible with the presence of a little amount of  $\text{MgAl}_2\text{O}_4$  spinel (density =  $3.6\text{ g cm}^{-3}$ ). Figure 5 shows a fracture of this sample; a practically dense material is obtained.

For the N2 (nitrates-TESPA) and Ci1 (citrate-TEOS) samples, a densification also occurs below  $1000^{\circ}\text{C}$ , but the shrinkage is less important and the final densities less. These powders do not densify completely at low temperatures.

The case of sample Ci2 (citrate-TESPA) is completely different (Fig. 6). The sample starts to shrink at  $820^{\circ}\text{C}$ , then expands considerably between 910 and  $960^{\circ}\text{C}$  (heating rate  $2^{\circ}\text{C min}^{-1}$  in this case). This expansion is produced by release of gas and a weight loss at the same temperature has been

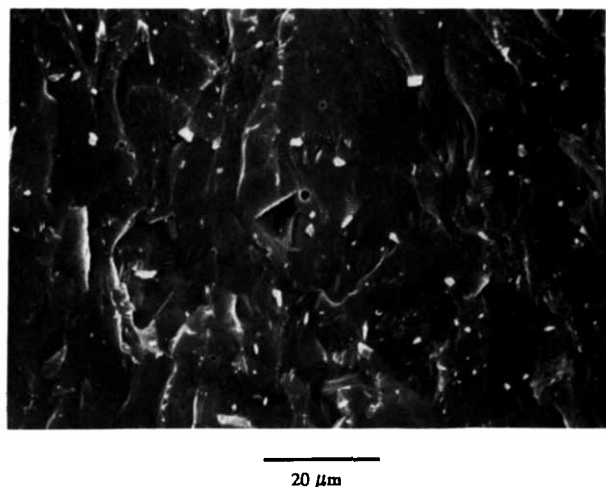


Fig. 5. Scanning electron micrograph showing a fracture of the N1 sample (nitrates-TEOS) annealed for 2 h at  $950^{\circ}\text{C}$ .

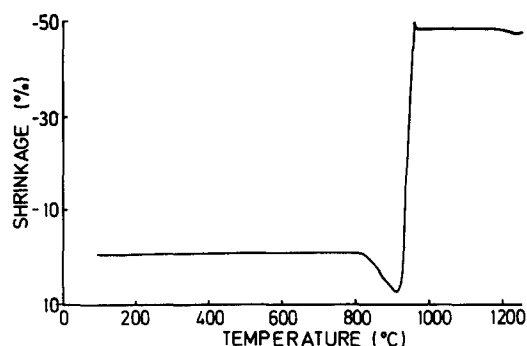


Fig. 6. Dilatometric curve of a Ci2 powder compact (citrate-TESPA); heating rate  $5^{\circ}\text{C min}^{-1}$  up to  $800^{\circ}\text{C}$ , then  $2^{\circ}\text{C min}^{-1}$ .

observed by TGA. A final expansion of 50% is obtained, for a white, very low density (density =  $0.2\text{--}0.3$ ) and porous material (Fig. 7), constituted of  $\alpha$ -cordierite but also of little amounts of  $\text{MgAl}_2\text{O}_4$  spinel, mullite and an unknown phase.

Therefore, as with mullite preparations, there are great differences between the cordierite powders elaborated in the same conditions but from different sources of cations, nitrates or citrates for Al and Mg, and TEOS or TESPA for Si. Complementary studies are necessary for understanding these results.

### 3.2 Alcoholic solutions

In alcohol, an organic gel having the same role than the polyacrylamide one in aqueous medium may also be made. Polyacrylamide, being insoluble in ethanol, is then replaced by poly(2-hydroxyethyl methacrylate (pHEMA). Only one solution, made by dissolving Al and Mg nitrates and TEOS in commercial ethanol (96%), has been tested for cordierite powder preparations.

A white powder is obtained, of much more dense aspect than those made from aqueous solutions

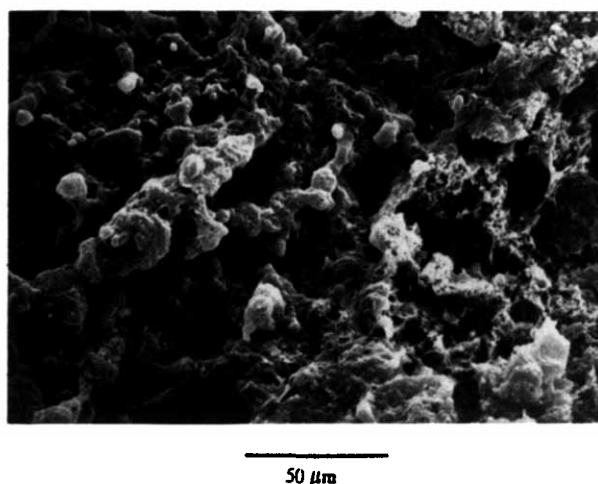


Fig. 7. Scanning electron micrograph showing the microstructure of the porous cordierite made from the Ci2 powder (citrate-TESPA).

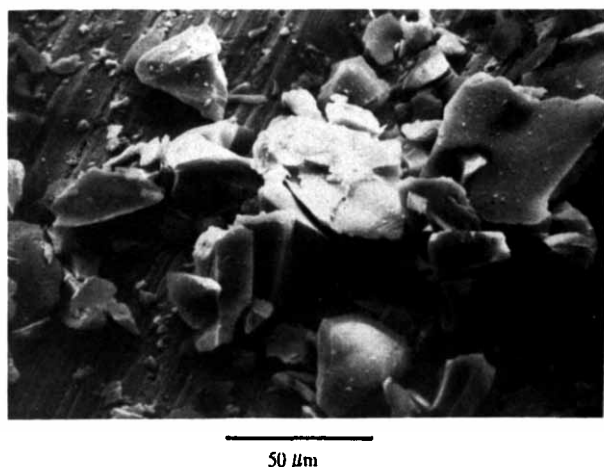


Fig. 8. Scanning electron micrograph showing the microstructure of the powder elaborated from Al and Mg nitrates and TEOS, in ethanol, pHEMA gel.

(Fig. 8). It is made of large porous blocks. The specific surface area is  $260 \text{ m}^2 \text{ g}^{-1}$ . Figure 9 represents the DSC curve of this powder. There is still a weak endothermic peak at  $840^\circ\text{C}$  attributed to the vitreous transition, followed by a weak exothermic peak at  $867^\circ\text{C}$  and then by an important exotherm at  $998^\circ\text{C}$ . The structural evolution, checked by XRD, shows that this exotherm corresponds to the crystallizations of both  $\mu$ - and  $\alpha$ -cordierites. At the beginning of the peak,  $\alpha$ -cordierite appears, in addition to the  $\mu$ -form. Figure 10 reports the XRD diagrams of the powder (a) after annealing at  $950^\circ\text{C}$  for 5 min, heating rate  $2^\circ\text{C min}^{-1}$  and (b) at the end of the exotherm. At  $950^\circ\text{C}$  there is already much  $\alpha$ -cordierite in addition to  $\mu$ -cordierite, and, at the end of the crystallization peak,  $\alpha$ -cordierite is the only phase present. The  $\text{MgAl}_2\text{O}_4$  spinel phase, always present in powders made from aqueous solutions, does not appear on the diagram. On the other hand, the obtention of pure  $\alpha$ -cordierite at so low a temperature expresses the great chemical homogeneity of this powder elaborated by this simple process. This powder densifies below  $1000^\circ\text{C}$ , and a density of  $2.44 \text{ g cm}^{-3}$  is obtained for a sample annealed for 2 h at  $950^\circ\text{C}$ .

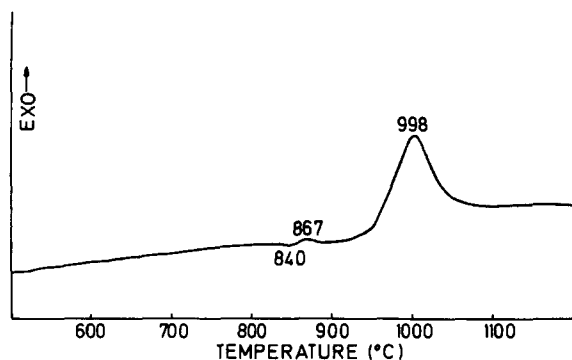


Fig. 9. DSC trace of the powder elaborated from Al and Mg nitrates and TEOS, in ethanol, pHEMA gel.

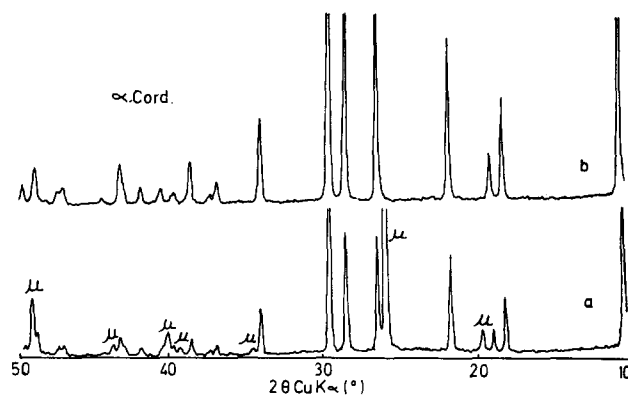


Fig. 10. XRD diagrams of the powder elaborated from Al and Mg nitrates and TEOS, in ethanol, pHEMA gel: a, after 5 min annealing at  $950^\circ\text{C}$ , heating rate  $2^\circ\text{C min}^{-1}$ ,  $\mu$ - and  $\alpha$ -cordierites; b, heated to  $1200^\circ\text{C}$  at  $10^\circ\text{C min}^{-1}$ ; pure  $\alpha$ -cordierite;  $\mu = \mu$ -cordierite.

#### 4 Conclusion

As for mullite, cordierite powders are easily obtained by the polyacrylamide gel process, from aqueous solutions, by using Si alkoxides as sources of silicon, but the properties of powders elaborated by the aqueous route are strongly dependent on the starting solutions. By an appropriate choice of the precursors, Al and Mg nitrates and TEOS, a powder which sinters completely by viscous flow before crystallizing is obtained by a simple aqueous process.

In the same way, from an ethanolic solution of the same precursors, simply gelled by poly(2-hydroxyethyl methacrylate), a very homogeneous powder is produced, and  $\alpha$ -cordierite is crystallized at lower temperature ( $1000^\circ\text{C}$ ).

The gelation of aqueous or organic precursor solutions by independent organic polymers, and further calcination of these gels, is thus a very attractive synthetic route to formation of very fine, homogeneous and reactive silico-aluminate powders.

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