

Spray-dried Homogeneous Cordierite and MLAS Glass–Ceramic Powders

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Abstract

Cordierite and MLAS glass–ceramic precursor powders have been obtained by spray-drying and calcination of aqueous sols made by hydrolysing tetraethylorthosilicate (TEOS) into nitrate solutions. The powders are amorphous and homogeneous but of reduced specific surface areas, and they expand instead of sintering beyond the glass transition temperature. Expanded ceramics are thus obtained.

If an organic polymer (polyacrylamide or polyvinyl alcohol) is added to the sol to be spray-dried, the surface areas are significantly increased, the chemical homogeneity still improved, and the compacted powders densify before crystallizing.

Ausgangspulver aus Kordierit und MLAS-Glas–Keramik Man erhielt durch Sprühtrocknen und durch Kalzinierung wässriger Lösungen, die durch die Hydrolyse von Tetraethylorthosilikaten in Nitrat-Lösungen hergestellt wurden. Die Pulver waren amorph und homogen aber durch abgeschwächte spezifische Oberflächenbereiche gekennzeichnet. Oberhalb der Glasbildungstemperatur quollen die Pulver auf anstatt zu sintern. Es wurden also auf diese Weise ausgedehnte Keramiken hergestellt.

Wird ein organisches Polymer (Polyacrylamid oder Polyvinyl-Alkohol) der Lösung für den Sprühtrockenprozeß zugesetzt, so nimmt der Anteil spezifischer Oberflächen signifikant zu, die chemische Homogenität wird verbessert und die kompaktierten Pulver können vollständig konsolidiert werden, bevor es zur Kristallisation kommt.

Des poudres précurseurs de vitrocéramiques, cordiérite et MLAS, ont été obtenues par atomisation à 200°C, puis calcination, de solutions aqueuses résultant de l'hydrolyse de l'orthosilicate d'éthyle (TEOS)

dans des solutions de nitrates. Les poudres sont chimiquement homogènes mais de faibles surfaces spécifiques. Elles gonflent au-dessus de la température de transition vitreuse au lieu de fritter et on obtient des céramiques expansées.

Si à la solution aqueuse on ajoute un polymère organique (polyacrylamide ou alcool polyvinylique), les surfaces spécifiques sont considérablement augmentées, l'homogénéité chimique est améliorée et les poudres compactées densifient complètement avant de cristalliser.

1 Introduction

Owing to their lower dielectric constant and thermal expansion coefficient than alumina or mullite, cordierite, $Mg_2Al_4Si_5O_{18}$, and cordierite-based glass–ceramics are promising materials for electronic packaging.^{1,2} Cordierite is also a selected material for the honeycomb support of catalysts in automobile exhaust gas treatment. However, cordierite ceramics are difficult to densify without sintering aids² when elaborated by the solid-state reaction of oxides. If the sintering of melt-quenched glass powder starts at low temperature, around 900°C, crystallization occurs rapidly and unfortunately stops this shrinkage, so hot pressing is necessary for the complete densification below 1000°C.³

Recent progress in processing chemistry has enabled the preparation of pure and amorphous cordierite powders which sinter at low temperature, below 1000°C, before crystallizing.⁴ The amorphous powder transforms first to a metastable phase, μ -cordierite, and, upon further heating, to the stable phase, α -cordierite. In contrast, in solid-state reaction μ -cordierite is not formed and the first

crystallized phase is spinel, MgAl_2O_4 , while α -cordierite is obtained only at much higher temperature by reaction of spinel with silica.

Several reports have appeared on the low-temperature sol-gel synthesis, from alcoholic solutions, of homogeneous cordierite powders. Metal alkoxide solutions have been used⁴⁻⁷ but a high degree of homogeneity is difficult to achieve because of differences in hydrolysis rates of the alkoxides. TEOS (tetraethylorthosilicate), the silicon alkoxide, may be partially hydrolysed prior to being mixed with the other alkoxides. In other preparations a chelating solvent has been used,⁸ the Mg alkoxide has been made from Mg powder⁹ or replaced by Mg nitrate,¹⁰ acetate¹¹⁻¹³ or chloride,¹⁴ sometimes in association with a chelated Al alkoxide.¹³⁻¹⁵

Recently a process has been described where the chemical homogeneity of multiple oxides is improved by gelling precursor aqueous solutions by an independent organic polymeric network: the polyacrylamide gel.¹⁶ The independent organic gels have also been revealed to be promising auxiliaries in processing homogeneous powders of mullite¹⁷ and cordierite¹⁸ from aqueous but also alcoholic solutions. For cordierite it was the first report of elaboration of low-temperature sinterable powders from aqueous solution. In this processing TEOS was hydrolysed in an aqueous solution of Al and Mg nitrates. The resulting solution was gelled by polyacrylamide and the gel calcined.

It has been noted that the chemical homogeneity of the cordierite powder is improved when the precursor aqueous solution is rapidly transformed into a powder.¹⁸ As a matter of fact, in acidic aqueous solutions, TEOS is hydrolysed into monomeric or oligomeric silanols which further condense and polymerize into silica gel, the kinetics of this evolution depending on pH, concentration and temperature.¹⁹ By gelling the solutions at room temperature and quickly transforming the gels into powders in a microwave oven the duration of the transitory step in hot aqueous solutions, where the formation of silica colloids is accelerated, is then reduced and more homogeneous powders are produced.

Rapid drying processes have been used by ceramists for a long time: spray-drying,^{20,21} thermal reactions of atomized solutions (TRAS),²² evaporative decomposition of solutions (EDS),²³ decomposition of misted solutions (DMS),²⁴ spray-drying and calcination process (SDC),²⁵ spray-pyrolysis,²⁶ etc. The rapidity in transforming the aqueous gels in processing cordierite being a critical point for the powder homogeneity, spray-drying has been used

for the elaboration of silicate powders from aqueous solutions. This paper gives some results obtained for cordierite and magnesium-lithium aluminosilicate (MLAS) glass-ceramic powders.

2 Experimental

Aluminium nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 98.5%, Merck, Darmstadt, FRG), magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%, Carlo Erba, Reuil Malmaison, France) and tetraethylorthosilicate (TEOS) ($\text{Si}(\text{OC}_2\text{H}_5)_4$, 98%, Merck) are the sources of Al, Mg and Si. TEOS is directly added to an aqueous solution of Al and Mg nitrates. The mixture is vigorously stirred until a clear aqueous solution is obtained. This is the precursor solution, containing around 0.06 equivalent $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ (35 g) per litre.

Cordierite precursor powder A is obtained by spray-drying this solution at 200–210°C with a Büchi 190 mini spray dryer (Flawil, Switzerland) (0.7 mm nozzle). The resulting powder is calcined in an aerated furnace to 750°C for 5 h.

Powder B is obtained under the same conditions after adding an aqueous solution of polyacrylamide to the precursor sol. To 215 ml of this sol (7.5 g of cordierite) 100 ml of solution containing 2 g of polyacrylamide are added. The polyacrylamide solution is made by polymerizing acrylamide in solution at 80–90°C using α, α' -azoisobutyronitrile (AIBN, Merck) as radical polymerization initiator (the average number M_n and weight M_w molecular weights, as measured by gel permeation chromatography, are respectively 9700 and 52 000).

Powder C is obtained as for powder B but after ageing the sol at room temperature for 5 weeks.

A powder with the composition $0.5\text{MgO} \cdot 0.5\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ has also been obtained from a solution made from Mg, Li and Al nitrates, and TEOS. To 440 ml of this solution, corresponding to 11.6 g of oxide powder, 50 ml of aqueous solution containing 2 g of a commercial polyvinyl alcohol (OSI, France, average molecular weight 50 000) are added. This sol is spray-dried as for the cordierite composition, and the resulting powder calcined at 2°C min⁻¹ to 600°C and held for 2.5 h at this temperature.

The crystalline structures were determined by X-ray diffraction (XRD) on a PW 1729 Philips diffractometer using CuK_α radiation. Differential thermal analysis (DTA) curves were obtained at 10°C min⁻¹ using Pt crucibles and approximately 250 mg of powder. Differential scanning calorimetry (DSC)

analyses were made at $10^{\circ}\text{C min}^{-1}$ with a high-temperature Setaram (Lyon, France) apparatus on 200 mg of powder. The specific surface areas of the powders were measured on a Micromeritics Flow-sorb II 2300 (Norcross, GA, USA) instrument by the BET method using nitrogen gas. The shrinkage of the powders, isostatically compacted at 200 MPa, was studied on a high-temperature Setaram dilatometer. A Cambridge Stereoscan 100 (Cambridge, UK) scanning electron microscope (SEM) was used to examine the size and shape of the spray-dried powders and the microstructures of the heat-treated samples.

3 Results and Discussion

3.1 Cordierite

As for the elaboration of cordierite powders by the aqueous route with polyacrylamide gel, TEOS is first reacted with an acidic aqueous solution of Al and Mg nitrates. With the aid of strong stirring the alkoxide is easily hydrolysed into monomeric and oligomeric silanols. At ambient temperature, acidic pH and low concentration the solution transformation into a sol and then into silica gel is slow.

3.1.1 Powder A

The precursor sol is spray-dried at $200\text{--}210^{\circ}\text{C}$. The resulting powder is made of inhomogeneously sized spherical particles (Fig. 1), their mean size, $5\text{--}15\ \mu\text{m}$, being typical of that obtained with such a technique. This powder is then directly heated in air at $2^{\circ}\text{C min}^{-1}$ to 750°C and held at this temperature for 5 h, or previously heated in a microwave oven before calcination. This thermal treatment does not modify

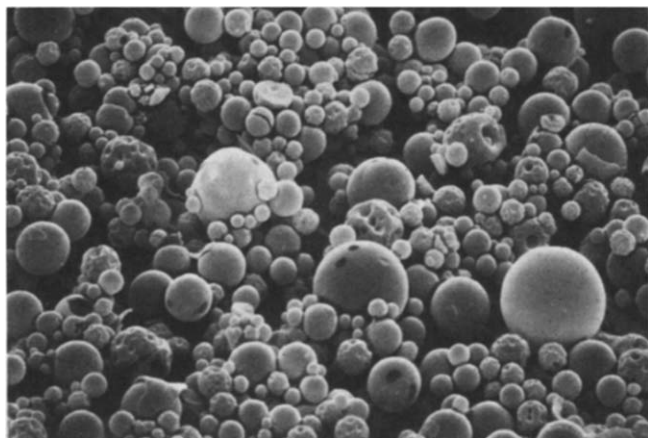


Fig. 1. SEM micrograph of cordierite powder A, spray-dried at 200°C .

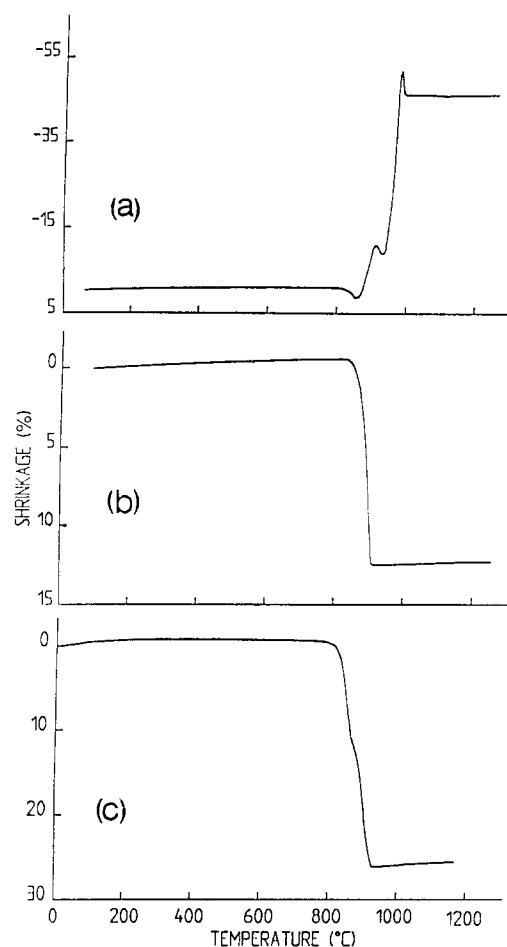
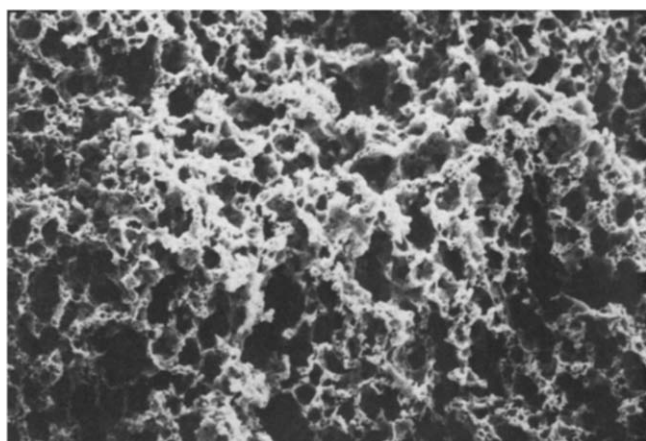


Fig. 2. Dilatometric curves of compacted samples; heating rate: $5^{\circ}\text{C min}^{-1}$. (a) Powder A, (b) powder A, annealed at 875°C for 2 h, (c) powder B.

the powder aspect. The specific surface areas were $8.7\ \text{m}^2\ \text{g}^{-1}$ for the powder treated in the microwave oven and $3.7\ \text{m}^2\ \text{g}^{-1}$ for the other powder.

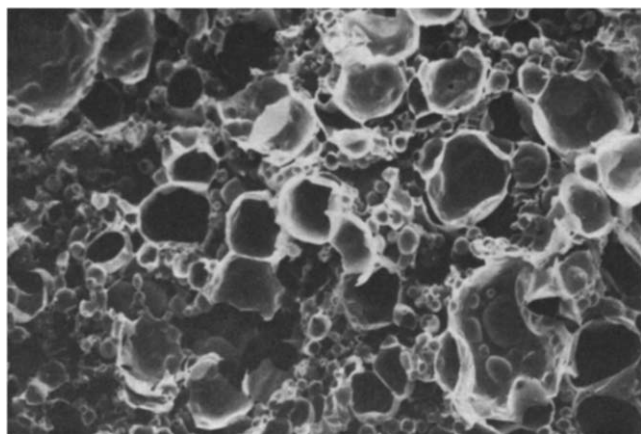
When the powder is compacted and studied by dilatometry it swells considerably instead of densifying (Fig. 2(a)). This expansion, occurring between 860 and 970°C , is accompanied by a gas release, as confirmed by thermogravimetric analysis. This means that the hollow spherical particles are not porous, and the entrapped gas resulting from thermal treatment can escape only at temperatures beyond the glass transition temperature of the cordierite glass (833°C). It has been observed that the expansion, for a given heating rate, is correlated with the specific surface area; it increases when the surface area decreases. In the case of Fig. 2(a) the dilatation reaches 50%, and an expanded and porous ceramic of very low density (around $0.3\ \text{g cm}^{-3}$) is obtained (Fig. 3).

The powders may be calcined to intermediate temperatures. For example, after annealing for 2 h at 875°C the particles were burst (Fig. 4). The powder is still mainly amorphous but with a beginning of



200 μm

Fig. 3. SEM microstructure of cordierite A ceramic, heated to 1300°C.



50 μm

Fig. 4. SEM micrograph of cordierite powder A, annealed at 875°C for 2 h.

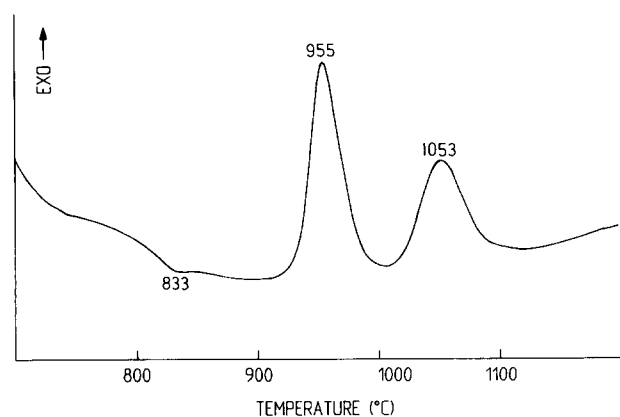


Fig. 5. DSC curve of cordierite powder A, after annealing at 875°C for 2 h; heating rate: 10°C min⁻¹.

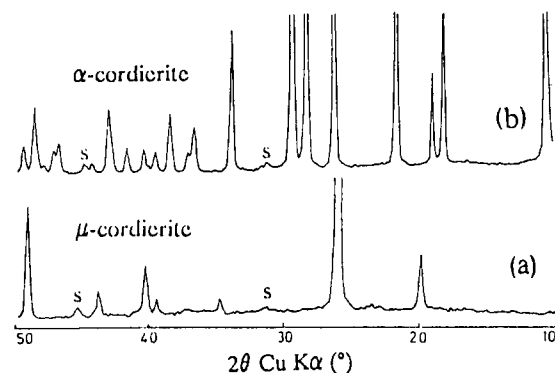


Fig. 6. XRD diagrams of cordierite powder A. (a) Heated to 980°C, (b) heated to 1350°C; heating rate: 10°C min⁻¹; S = MgAl₂O₄.

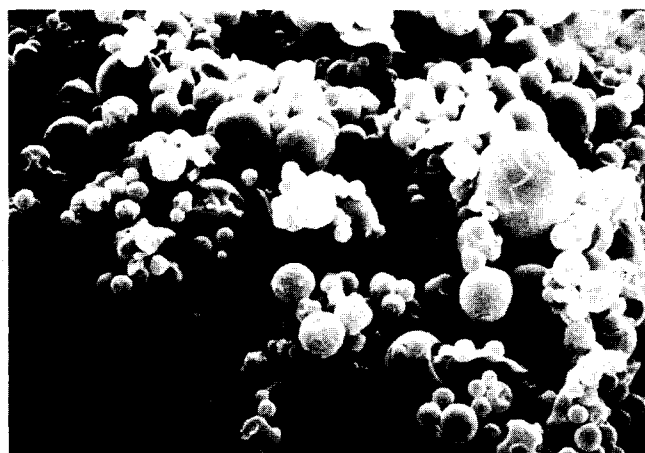
crystallization of μ -cordierite. Figure 5 represents the DSC curve of this powder at a heating rate of 10°C min⁻¹. There is one endothermic peak (833°C) attributed to the glass transition T_g , and two exothermic peaks whose maxima are at 955 and 1053°C. The first corresponds to the crystallization into the metastable μ -cordierite, and the second to the conversion of μ -cordierite into the stable α -cordierite phase. Figure 6 represents the XRD diagrams after heating to 980 and 1350°C. At 980°C the pattern is that of μ -cordierite, and at 1350°C that of well crystallized α -cordierite. These crystalline phases are nearly pure; the only apparent secondary phase is MgAl₂O₄ spinel (detected by the $2\theta = 31.3^\circ$ and 44.9° peaks).

The powder annealed at 875°C for 2 h has been studied by dilatometry, after being slightly ground and compacted (Fig. 2(b)). Heated at 5°C min⁻¹ the sample densifies between 835 and 910°C. The final density obtained for this sample does not exceed 80% of the theoretical density, but an optimization of previous thermal treatment and deagglomeration should improve it.

So, by this extremely simple process, an amorphous homogeneous powder is obtained, which crystallizes to an expanded cordierite of low density, or, after appropriate thermal and mechanical treatments, densifies at low temperature (below 1000°C) before crystallizing to α -cordierite via μ -cordierite.

3.1.2 Powder B

Powder B was obtained under the same conditions and from the same precursor solution as powder A but after adding an aqueous solution of polyacrylamide. Spray-dried powders, calcined at 2°C min⁻¹ to 750°C, do not appear very different from powder A, spray-dried without organic polymer (Fig. 7). A great difference is, however, found for the specific



20 μm

Fig. 7. SEM micrograph of cordierite powder B, annealed at 750°C for 5 h.

surface area; after calcining at 750°C for 5 h it is 260 m² g⁻¹, that is in the order of 50 times that of powder A. The spherical particles are thus porous. The behaviour in shrinkage is different (Fig. 2(c)) compared with powder A under the same conditions (Fig. 2(a)). After compaction the sample densifies between 800 and 930°C by heating at 5°C min⁻¹. Final densities are 98% of the theoretical (2.512 g cm⁻³ for α -cordierite, JCPDS X-ray diffraction file) for samples annealed 2 h at 950°C.

The DTA curve of powder B is represented in Fig. 8. At 10°C min⁻¹ there is a T_g endothermic peak at 834°C, followed by a weak exotherm. At higher temperatures there is only one crystallization exotherm, rather strong, at 980°C. The structural evolution of the powder has been checked by XRD. Until this peak the powder remains amorphous. At the beginning of the crystallization peak it remains an amorphous phase in addition to μ -cordierite, and α -cordierite has already begun to crystallize. For the sample quenched just after 980°C (top of the peak) the two polymorphs μ and α are present (Fig. 9). For

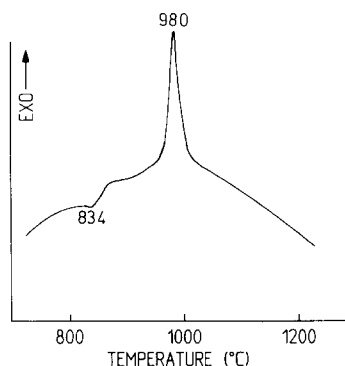


Fig. 8. DTA curve of cordierite powder B; heating rate: 10°C min⁻¹.

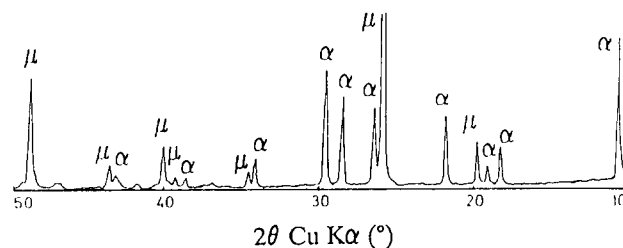


Fig. 9. XRD diagram of cordierite B, heated to 980°C at 10°C min⁻¹. α = α -Cordierite, μ = μ -cordierite.

a sample annealed for 2 h at 950°C a small amount of μ -cordierite remains, and when calcined to 1000°C or higher a single α -cordierite phase is obtained. No trace of secondary phase appears on the XRD diagrams, and the conversion of μ - to α -cordierite occurs on a very narrow temperature scale, and possibly one part of the powder may crystallize directly to α -cordierite.

A cordierite gel is considered to be homogeneous at the atomic level if it crystallizes to α -cordierite only via μ -cordierite.¹⁵ In the present case powder B is homogeneous, and it should be added that the temperature difference between μ - and α -cordierite crystallization temperatures may be an additional indication of the chemical homogeneity of the powder. The greater this homogeneity, the lower the temperature at which α -cordierite will crystallize. Complementary studies are necessary for a better understanding of the chemistry of the powder transformation.

Transient additives have been investigated in an effort to modify the characteristics of ceramic powders prepared by thermal reaction of atomized solutions.²² The use of additives was suggested to prevent interparticle sintering of the fine crystallites and to result in an increase in surface area. Ammonium chloride, polyvinyl alcohol, glycerin and polyethylene glycol have been used and, for crystallized powders, it was found that the specific surface area generally increases. High molecular weight polymers have also been added for achieving an adequate viscosity that allows spinning of Zr acetate solution and drawing fibres.²⁷ In the case of silicate powder elaboration Kanzaki *et al.*²⁸ spray-pyrolysed at 350–650°C a mullite precursor solution made by dissolving Al nitrate and TEOS in water-methanol (1:1 by volume) mixed solvent. The powder was very homogeneous and crystallized completely to orthorhombic mullite at 970°C. However, the specific surface area was rather limited (15 m² g⁻¹ at 650°C) compared with that usually measured for powders obtained by the sol-gel method. In the case of cordierite the addition of water-soluble organic polymer to the aqueous

precursor solution to be spray-dried has a spectacular effect on the powders. The hollow spherical particles are porous, the surface areas much more important, the chemical homogeneity is improved, and the compacted powders sinter at low temperature. The role of the organic additives may be assumed to increase the viscosity during the drying step, thus preserving a better mixing of the cations, and to create porosities in the particle shells during their further thermal decomposition.

However, it seems that the molecular weight of the added polymer, its nature and its concentration, in addition to previous thermal treatment, play an important role on the structural evolution versus temperature. If the optimal chemical homogeneity is expressed by a single crystallization peak on the DTA curve, this is not always obtained, and two distinct peaks, though close, occur for other powders elaborated by spray-drying organic polymer containing solutions. It has also been observed that the precursor powder, crystallizing to α -cordierite via a single DTA peak, thus *a priori* the most homogeneous, changes with time, even at room temperature, after being calcined at 750°C for 5 h. The crystallizations to μ - and α -cordierites are well separated after a few weeks. The freshly prepared powder would be in a metastable state, and a slow internal reorganization of the atoms would occur so as to favour the crystallization of μ -cordierite on further heating, as is usually observed for homogeneous cordierite powders. It has also been noted that the crystallization temperature of α -cordierite may depend on the powder compaction pressure. All these observations implicate further extensive studies.

3.1.3 Powder C

Powder C was obtained under the same conditions and from the same precursor sol than powder B but after ageing for 5 weeks. The powder looks like powder B, but the structural evolution versus temperature is different. There are two crystallization peaks, whose maxima are separated by 134 K (Fig. 10). The powder crystallizes first to μ -cordierite and the conversion to α -cordierite occurs at much higher temperature than for powder B, and traces of MgAl_2O_4 phase appear again on the XRD diagrams. This powder is less homogeneous. This would result from the evolution of the monomeric and oligomeric silanols produced by the TEOS hydrolysis in acidic aqueous solution. These silanols condense to a silica sol. Although the condensation and polymerization reactions are slow in diluted acidic solutions, after 5 weeks at room temperature,

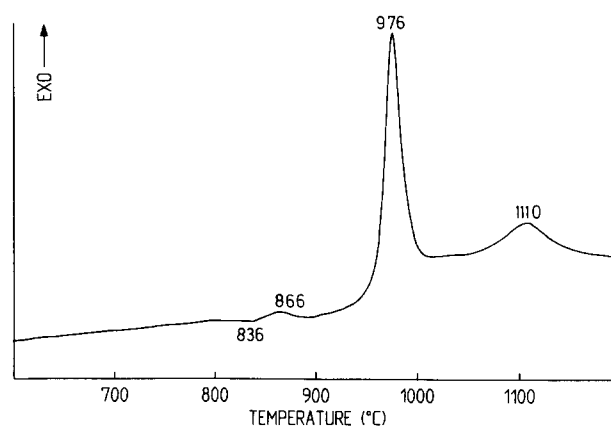


Fig. 10. DSC curve of cordierite powder C; heating rate: 10°C min⁻¹.

the solution had changed to a slightly opalescent sol. However, the rapidity in the transformation of the sol into a powder by spray-drying allows the obtention of rather homogeneous powders crystallizing to α -cordierite via μ -cordierite. These powders also densify at low temperature before crystallizing.

3.2 MLAS powder

Another composition of glass-ceramic powder has also been elaborated by the same spray-drying technique: 0.5MgO.0.5Li₂O.Al₂O₃.4SiO₂. The aqueous solution is made from Mg, Li and Al nitrates, and TEOS. The added hydrosoluble polymer is a commercial poly(vinyl alcohol) (average

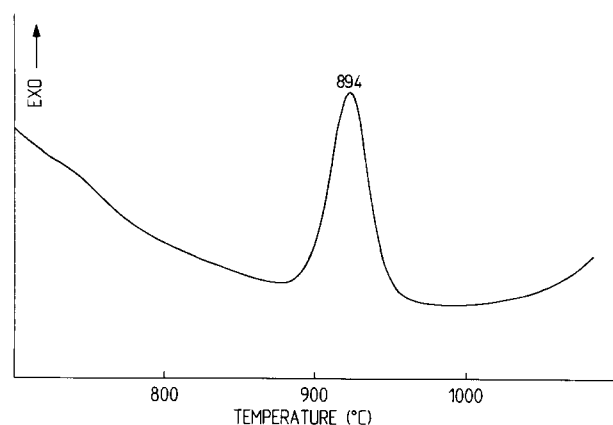


Fig. 11. DSC curve of MLAS powder; heating rate: 10°C min⁻¹.

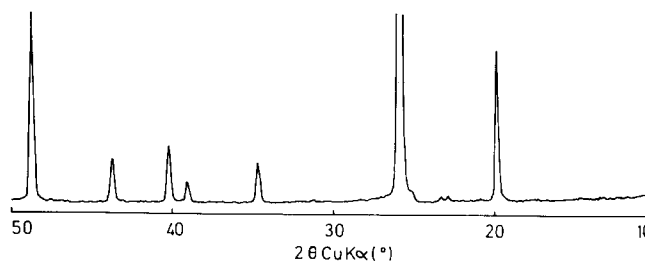


Fig. 12. XRD diagram of MLAS ceramic, heated to 1000°C at 10°C min⁻¹.

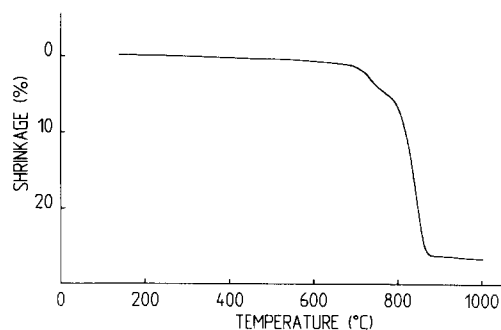


Fig. 13. Dilatometric curve of compacted MLAS powder; heating rate: 5 C min^{-1} .

molecular weight 50 000). The solution is spray-dried at 200°C as for cordierite, and the powder is calcined at $2^{\circ}\text{C min}^{-1}$ to 600°C for 2.5 h. A white powder is obtained.

The DSC analysis of this powder, at $10^{\circ}\text{C min}^{-1}$ (Fig. 11), presents one exotherm with its beginning at 872°C and its top at 894°C . This peak is related to the crystallization to a β -quartz solid solution, like the μ -cordierite phase (Fig. 12). This powder, after compaction at 200 MPa and heated at $5^{\circ}\text{C min}^{-1}$, densifies below 860°C (Fig. 13). For comparison, by spray-drying the precursor solution without organic polymer, a powder is obtained which crystallizes to the same phase but expands instead of sintering. The behaviour is like that of cordierite. Poly(vinyl alcohol) is also efficient in spray-drying cordierite powders, and very homogeneous powders have also been obtained using this polymer.

4 Conclusion

Spray-drying is a very simple process for the elaboration of homogeneous glass-ceramic powders, at least for cordierite and the studied MLAS composition. The precursor aqueous solutions are easily made from nitrates and TEOS. Only the addition of organic polymer to the solutions to be spray-dried makes the resulting powders chemically more homogeneous and the spherical particles porous, and consequently densification occurs naturally before crystallization.

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