

Synthesis and formation mechanism of submicrometre spherical cordierite powders by ultrasonic spray pyrolysis

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Cordierite powders containing very pure submicrometre spherical particles have been synthesized by the ultrasonic spray pyrolysis. Aqueous solutions of silicic acid, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ were used as precursors. Scanning electron micrographs have shown that particle surfaces were smooth and the mean particle diameter was $0.834 \mu\text{m}$. For the estimation of chemical and phase composition and phase transformation temperatures, differential thermal analysis, thermogravimetric analysis, X-ray diffraction, energy dispersive spectroscopy and infrared analysis have been applied. It was found that during spray pyrolysis, the condensation of silicic acid mostly occurred while aluminium and magnesium ion remained incorporated between Si–O–Si chains. By subsequent heating to over 800°C , Si–O–M bonds ($\text{M} = \text{Al}, \text{Mg}$) were formed. The synthesis of cordierite occurred by the crystallization of μ -cordierite from the amorphous phase at 900°C followed by the phase transformation of μ - into α -cordierite in the temperature range 1100 – 1200°C .

1. Introduction

Owing to the small coefficient of thermal expansion (1×10^{-6} – $4 \times 10^{-6}^\circ\text{C}^{-1}$ in the temperature range 25 – 800°C), high thermal shock stability, low dielectric constant ($\epsilon = 4$ – 6) and high volume resistivity ($> 10^{14} \Omega\text{cm}$), cordierite ceramics have been applied for the fabrication of electric heater supports and the supports of catalysers for the conversion of combustion gases from engines [1]. Recently, both cordierite ceramics and vitroceraamics have become very promising for producing substrates for high integral circuits and microchips, owing to the compatibility of their coefficients of thermal expansion with that of silicon and the possibility of co-sintering with copper [2].

Much research has been devoted to advanced methods of powder synthesis from solutions, enabling the fabrication of highly homogeneous cordierite powders which can be sintered at much lower temperatures than is usual. One of these techniques is the alkoxide sol–gel method. Disadvantages of this method are the relatively high price of starting compounds and solvents, as well as the great difference between the rates of hydrolysis of alkoxides, making powder synthesis more difficult and more expensive. The sol–gel method also includes drying and calcination of the gel. In these homogeneous gels, Si–O–M ($\text{M} = \text{Al}, \text{Mg}$) bonds are formed immediately after the hydrolysis of the initial compounds is completed. This results in the crystallization of μ -cordierite in the tem-

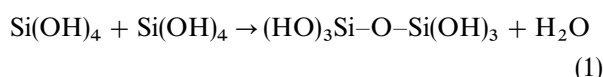
perature range 850 – 1000°C . The phase transformation of μ - into α -cordierite occurs in the temperature range 1000 – 1200°C . In the case of the less homogeneous gels, the synthesis of cordierite occurs usually by the crystallization of spinel phase and by its reaction with amorphous SiO_2 at temperatures over 1200°C [3–10].

The synthesis of powders by ultrasonic spray pyrolysis enables very homogeneous powders to be produced directly from the solutions sprayed inside the reactor. During pyrolysis, the sprayed droplets are transformed into microporous or dense particles by different processes, including solvent evaporation, the precipitation of dissolved substance, drying, the thermolysis of precipitated particles and finally sintering. As a result of the high rates of these processes, the high homogeneity of the initial solution is retained in the obtained particles. The advantages of this method of powder synthesis are that all the mentioned processes occur in one step, and also each droplet/particle is subject to the same reaction conditions and no subsequent milling is necessary. By control of process parameters, the concentration, pH value, homogeneity of the initial solution, the type of precursor, temperature gradient and residence time of the droplet/particle inside the reactor, it is possible to influence directly the morphology, particle-size distribution, homogeneity and phase composition of the particles [11–17].

Because there are practically no data about the synthesis of cordierite by ultrasonic spray pyrolysis, the goal of this work was to produce submicrometre cordierite powder by ultrasonic spray pyrolysis starting from cheap compounds such as silicic acid, magnesium and aluminium salts, and to characterize the obtained powder, whilst studying the formation mechanism of particles and phases during heating.

2. Experimental procedure

For the synthesis of cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) powder, the 0.01 M solution was prepared by dissolving $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in an aqueous solution of silicic acid. Silicic acid was obtained by passing sodium silicate through a column filled with cation exchanger in H^+ form, where the exchange of Na^+ ions, from sodium silicate with H^+ ions occurred. To prevent the dissociation of silanol groups and the condensation of silicic acid according to the equation



a 3% solution of silicon acid with $\text{pH} = 2.8$, corresponding to the point of zero charge, was used.

The atomization was performed using an ultrasonic atomizer Gapsol-RBI-9001 with a resonant frequency of 2.5 MHz and a capacity of 400 ml h^{-1} . The obtained aerosol droplets of about $2 \mu\text{m}$ diameter were introduced in an air flow of $30\text{--}40 \text{ l h}^{-1}$ into the reactor at 900°C . The residence time of droplet/particle inside the reactor was 95 s, assuming that the rate of the supporting gas and the rate of the droplet are the same. Under these conditions, the heating rate was 18°C s^{-1} . The powder was obtained in the collecting chamber at the end of the reactor. The equipment for the powder synthesis is shown in Fig. 1.

The analysis of morphology and particle sizes after spray pyrolysis, as well as after heating at 1300°C , was done using a scanning electron microscope Jeol-JSM 5300 at a cathode voltage of 25–30 kV followed by analysis of micrographs by means of the semiautomatic image analyzer Video Plan, Kontron. Powders

were prepared by deagglomeration in ethanol using ultrasonic waves followed by carbon deposition. The chemical composition was estimated by energy dispersive spectroscopy (EDS), Oxford Instruments QX-2000 in the X-ray range of 0.5–20 keV. Differential thermal and thermogravimetric analysis (DTA and TGA) were done using a MOM-Derivatograf C at temperatures up to 1300°C with a heating rate of $15^\circ\text{C min}^{-1}$ in air. The phase composition, i.e. phase transformations of both powders after spray pyrolysis and powders heated at 900°C , 1000°C , 1100°C , 1200°C and 1300°C were registered using a diffractometer (Siemens D500) with CuK_α radiation with the angles of $2\theta = 5\text{--}60^\circ$ and 0.02 step and an infrared (IR) spectrometer (Perkin-Elmer 782) in the range of wave numbers $400\text{--}1600 \text{ cm}^{-1}$ with the sample preparation according to the KBr method at the sample to and KBr ratio of 1:100.

3. Results and discussion

3.1. The morphology and quantitative stereological analysis of particles

Scanning electron micrographs of cordierite particles obtained by spray pyrolysis are given in Fig. 2. The presence of non-agglomerated particles of high sphericity and mostly submicrometre sizes is evident. The particle surface is smooth as a result of aluminium nitrate melting at 76°C and also the influence of surface tension on the droplet, because of homogeneous distribution of silicic acid and its uniform condensation in all directions [18]. Particles with larger diameters ($1\text{--}3 \mu\text{m}$) are registered at the same time. It is assumed that they are formed as a consequence of droplet coalescence during spray pyrolysis. Plane surfaces of particles are the result of collision and agglomeration during particle formation from the droplets.

It is evident from scanning electron micrographs of the powder heated at 1300°C at a heating rate of $15^\circ\text{C min}^{-1}$ (Fig. 3) that most of the spherical particles have submicrometre sizes. In the case of a small number of particles, fragmentation has occurred and they have been formed by the mechanism of surface precipitation. Most of the particles have remained

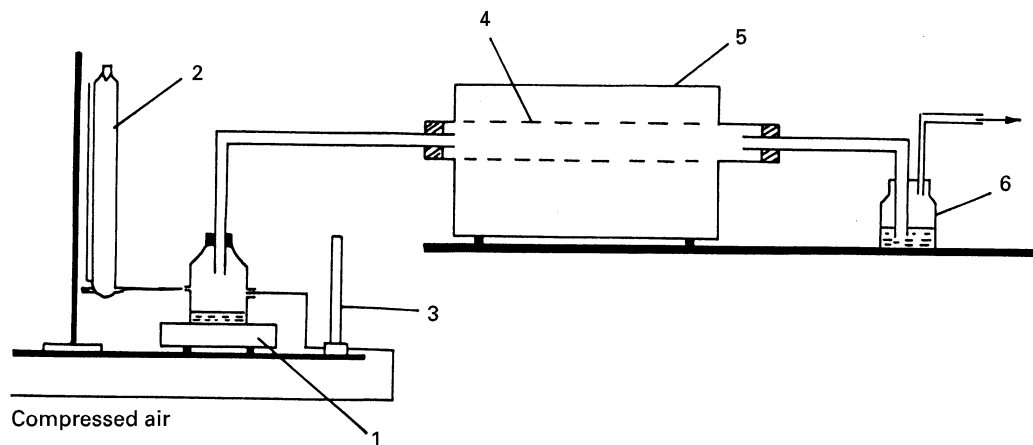


Figure 1 Equipment for powder synthesis by ultrasonic spray pyrolysis. 1, Aerosol generator (Gapsol 9001 type, RBI); 2, constant level vessel; 3, flow meter; 4, quartz tube (40 mm diameter); 5, tubular furnace (Heraeus ROF 7/50); 6, collecting chamber.

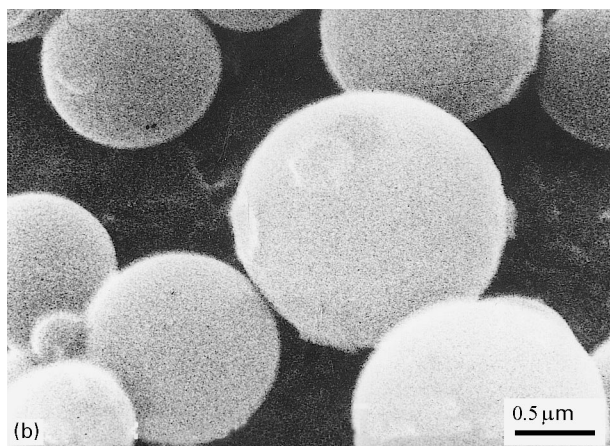
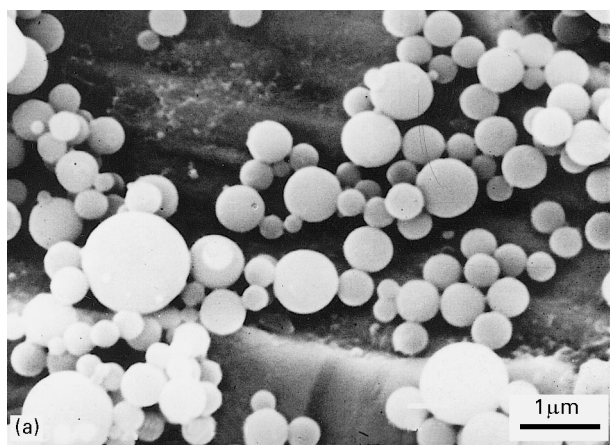


Figure 2 (a,b) Scanning electron micrographs of the cordierite powder obtained by ultrasonic spray pyrolysis.

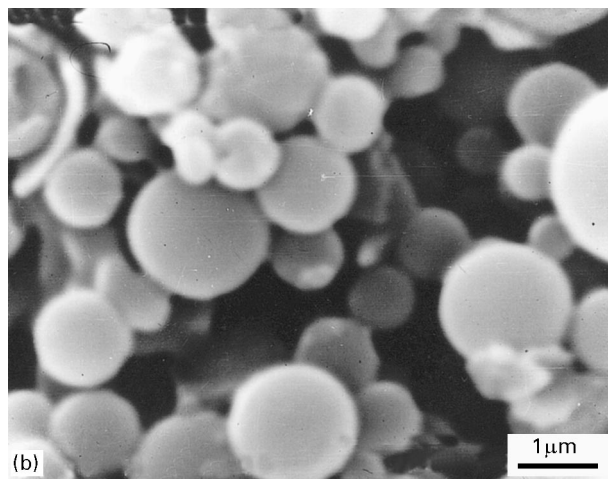
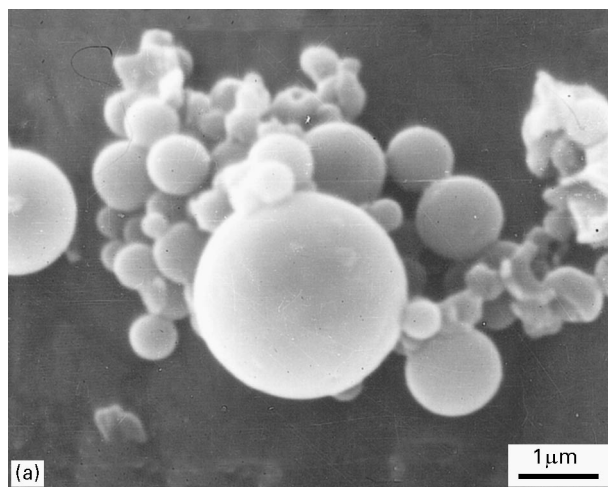


Figure 3 (a,b) Scanning electron micrographs of the cordierite powder heated up to 1300 °C at a heating rate of 15 °C min⁻¹.

unchanged and it is assumed that they have been formed by the mechanism of volume precipitation. The fragmentation of particles has not occurred owing to the porosity and open structure of SiO₂ particles, which are the consequence of condensation of silicic acid, that occurs at a given concentration and pH of the solution. It results in open-branch chain-like particles [19]. Such an open structure enables the intensive evaporation of water and gases obtained by the decomposition of salts, without fragmentation of particles, in spite of the high temperature gradient in the reactor.

On the basis of the results of quantitative stereological analysis (Table I) we can see that the produced powders contain submicrometre particles of high sphericity. The apparent increase in mean particle diameter of the powder heated at 1300 °C is the result of the diameter calculation using a smaller number of

particles. A narrow particle-size distribution is evident in Fig. 4.

3.2. The estimation of chemical composition and phase transformation

3.2.1. EDS analysis

Analysis of the powder produced by spray pyrolysis by energy dispersive spectroscopy (EDS) (Fig. 5) shows the presence of atoms of aluminium, silicon and chlorine. The presence of chlorine atoms indicates that the calcination is not completed because of a too short residence time of particles inside the reactor. Nitrogen from nitrate ions and magnesium as the constitutive element could not be registered by the applied measurement technique.

TABLE I Statistical analysis of powder geometric parameters synthesized by spray pyrolysis (1) and thermally treated at 1300 °C (2)

Sample	Section area (μm ²)			Perimeter (μm)			Perimeter form factor			Area form factor			Diameter (μm)			Standard deviation
	Min.	Max.	Mid.	Min.	Max.	Mid.	Min.	Max.	Mid.	Min.	Max.	Mid.	Min.	Max.	Mid.	
1	0.05	4.90	0.65	0.77	7.92	2.72	0.66	1.01	0.95	0.97	1.02	0.99	0.24	2.55	0.83	0.308
2	0.15	12.34	0.87	1.42	12.60	2.91	0.72	1.01	0.96	0.98	1.01	0.99	0.44	3.93	0.91	0.540

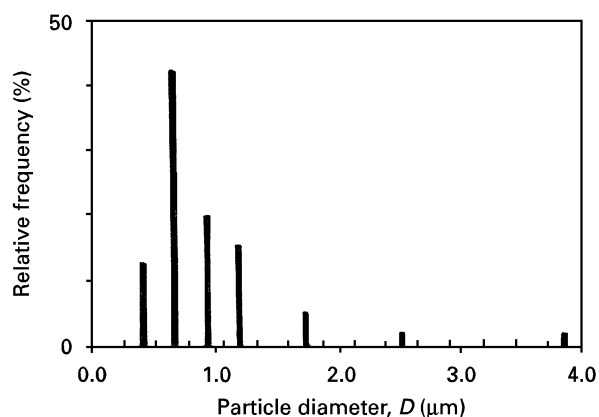


Figure 4 Particle-size distribution of the cordierite powder obtained by ultrasonic spray pyrolysis.

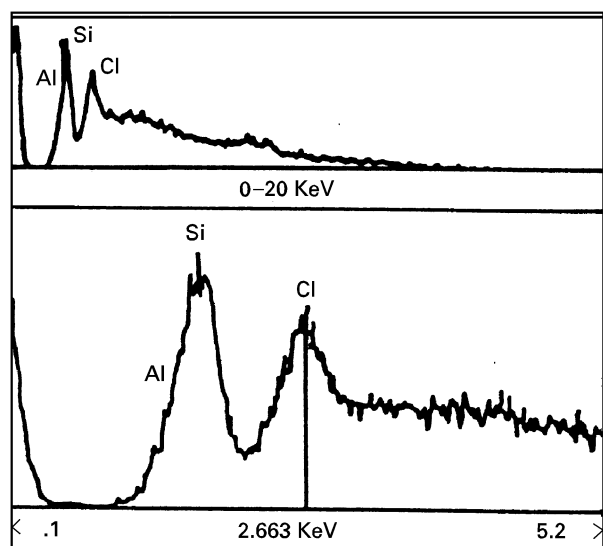


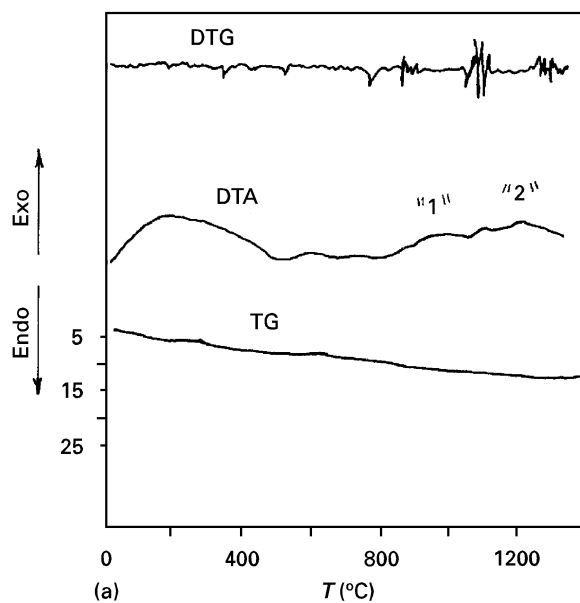
Figure 5 EDS analysis of the cordierite powder obtained by ultrasonic spray pyrolysis.

3.2.2. DTA and TGA

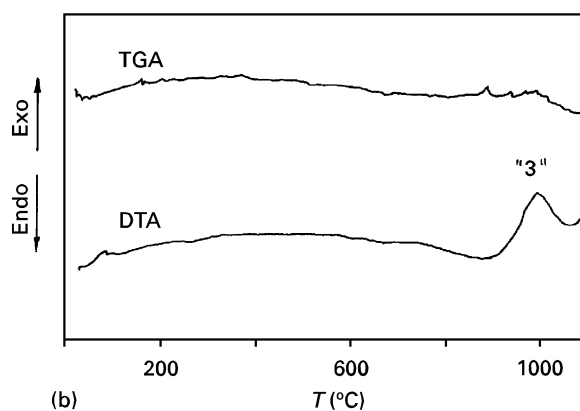
DTA and TGA of both powders obtained by spray pyrolysis at 1300 °C and the powder which had been previously heated at 800 °C in 2 h are given in Fig. 6a and b, respectively. Previous heating of the powder was done to eliminate all products of thermal decomposition and thus to enable better registration of the onset and the end of phase transformations. A few slight peaks in the range 900–1200 °C are characteristic for data shown in Fig. 6a. The exothermal peak “1” in the range 900–1000 °C may be the result of the crystallization of μ -cordierite, and peak “2” in the range 1000–1200 °C may be the consequence of the phase transformation of μ - into α -cordierite. It is obvious from Fig. 6b that in the temperature range 900–1030 °C, peak “3” appears. This could be explained as a consequence of the crystallization of μ -cordierite [3–10].

3.2.3. X-ray analysis

Diffractograms of powders produced by spray pyrolysis and powders subsequently heated at 900, 1000,



(a)



(b)

Figure 6 DTA and TGA of the cordierite powder (a) obtained by spray pyrolysis, (b) previously heated at 800 °C for 2 h.

1100, 1200 and 1300 °C are given in Fig. 7. The diffractogram of the powder heated at 900 °C shows diffraction peaks at $d = 0.343$, 0.226 and 0.186 nm which correspond to μ -cordierite according to the ASTM card 14-249. It is in accordance with the results of DTA. The peak at $d = 0.201$ nm corresponds to Al, Mg-spinel according to ASTM card 21-1152. In the case of the sample heated at 1000 °C, other diffraction peaks of μ -cordierite appear at $d = 0.445$ and 0.160 nm, and the previous peaks become more intense compared to the peaks of the sample heated at 900 °C. New peaks of Al, Mg-spinel are also obvious at $d = 0.286$ and 0.243 nm. In the case of the sample heated at 1100 °C the crystallinity of μ -cordierite and spinel is better and very slight diffraction peaks, corresponding to mullite according to ASTM card 15-776, are registered. At 1200 °C, diffraction peaks characteristic of α -cordierite appear according to ASTM card 13-293. Thus the phase transformation of μ -cordierite into α -phase occurs in the temperature range 1100–1200 °C. It is complementary with the DTA data. In the case of the sample heated at 1300 °C, a higher degree of crystallinity of α -cordierite is evident. Al, Mg-spinel and mullite are still present, but in

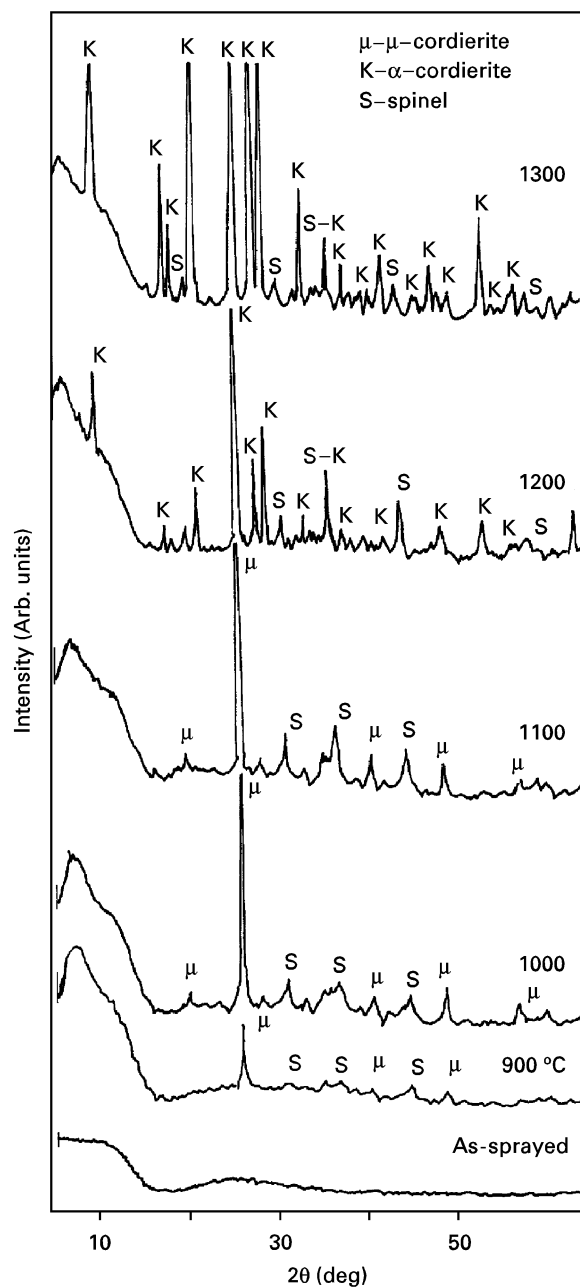


Figure 7 Diffractograms of the cordierite powder obtained by ultrasonic spray pyrolysis and subsequently heated at 900 °C, 1000 °C, 1100 °C, 1200 °C and 1300 °C for 2 h.

small amounts, that becomes obvious if we compare their peaks with cordierite peaks.

3.2.4. IR analysis

The results of IR analysis are shown in Fig. 8. In the case of samples obtained by spray pyrolysis and dried at 150 °C, absorption bands appear at 1090, 940 and 470 cm^{-1} , corresponding to the vibrations of Si–O bonds in amorphous silica. The absorption band at 800 cm^{-1} corresponds to the ring structure of the SiO_4 tetrahedron, indicating higher degree of condensation of silicic acid. IR spectra of the samples heated at 800 and 900 °C are similar to the spectrum of cordierite glass. In the case of the sample heated at 1000 °C, a wider adsorption band appears at 700–750 cm^{-1} , that probably corresponds to the

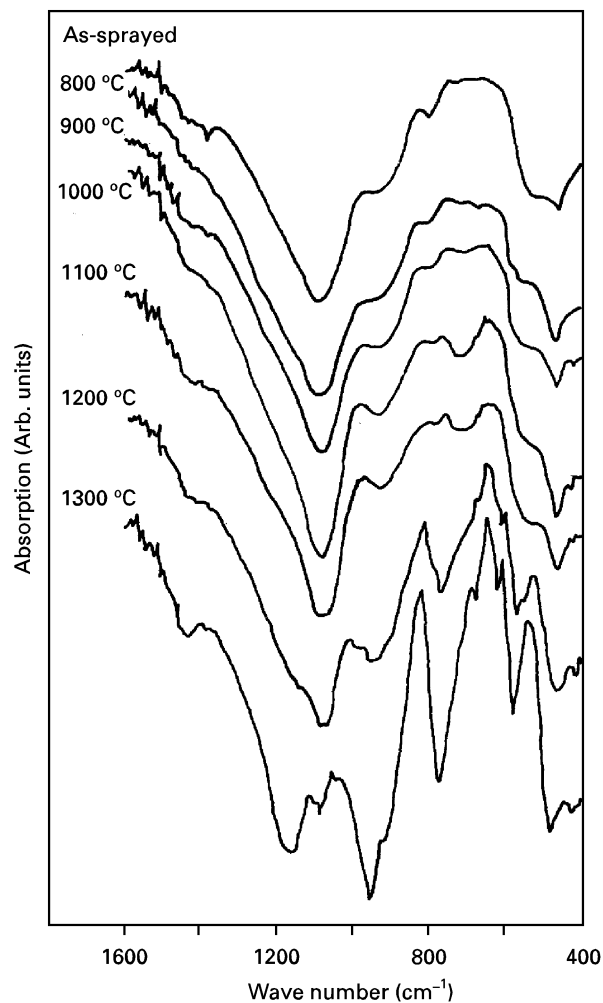


Figure 8 IR analysis of the cordierite powder obtained by ultrasonic spray pyrolysis and subsequently heated at 900 °C, 1000 °C, 1100 °C, 1200 °C and 1300 °C for 2 h.

vibrations of M–O bonds (M = Al, Mg) indicating Si–O–M bonding [5]. Owing to the appearance of these bonds just in the temperature range 900–1100 °C, it is concluded that Si–O–M bonds, characteristic of a very homogeneous system, are not formed either in the initial solution or in the droplet/particle [3–10]. On the bases of all these data it is obvious that during the particle formation, first the silicic acid is condensed and branchy Si–O–Si chains are formed [19]. Hydrated ions of aluminium and magnesium remain incorporated between these chains. At temperatures over 800 °C these ions start to be connected with the Si–O–Si net and Si–O–M bonds are formed. At the same time, the reaction of ions which form spinel also occurs, which can explain the appearance of absorption bands at 700 and 530 cm^{-1} , corresponding to spinel, registered by X-ray analysis. In the case of the sample heated at 1100 °C there are no significant differences between the IR spectrum and the IR spectrum at 1000 °C. After further heating at 1200 °C the band at 780 cm^{-1} , corresponding to the ring structure of the SiO_4 tetrahedron, has appeared. In the case of the sample heated at 1300 °C, intensive bands at 1175 and 1140 cm^{-1} , as well as doublet bands at 435 and 415 cm^{-1} , have been

registered. They are characteristic of well-ordered cordierite structure [20].

4. Conclusion

Submicrometre spherical cordierite powder of high purity was synthesized by spray pyrolysis. Si–O–Si chains were found to be formed during spray pyrolysis. Hydrated ions of aluminium and magnesium, as well as the remaining chloride and nitrate ions, are incorporated between Si–O–Si chains. Owing to subsequent heating, the reaction between Si–O–Si chains and the mentioned ions occurs, resulting in Si–O–M bonds (M = Al, Mg) and in the formation of both μ -cordierite and spinel. The crystallization of μ -cordierite from the amorphous phase has been registered at 900 °C and the phase transformation of μ - into α -cordierite occurs in the temperature range 1100–1200 °C. Although the temperature gradient during thermal decomposition of the aerosol has been large, the produced spherical particles remained unchanged, owing to the high permeability of the branchy chain-like net of SiO₂ for the gases formed by the decomposition of the initial compounds.

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