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New Aqueous Mullite Precursor Synthesis. Structural Study by ^{27}Al and ^{29}Si NMR Spectroscopy

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Abstract

A mullite precursor gel is prepared by the slow and homogeneous generation of ammonia inside an aqueous solution of aluminium nitrate and silicic acid, urea being used as the base generator. At 80–100°C a silica gel is rapidly formed, by a catalytic reaction, and then this gel is slowly digested by the partially hydrolysed aluminium atoms which link to silica by Si–O–Al bonds. The structural evolution has been studied by ^{27}Al and ^{29}Si NMR spectroscopy. The first aluminium atoms are incorporated in tetrahedral symmetry and the following ones remain hexacoordinated. The system evolves to soluble aluminosilicate colloids with a local structure close to that of imogolite or allophane: each silicon atom being linked to three AlO_6 hexahedra and a hydroxyl group. By the completion of the hydrolysis the colloids are cross linked to a gel precursor of mullite. With thermal treatment the imogolite-like orthosilicate units arrangement is rapidly lost, but the xerogel remains chemically homogeneous with a random distribution of Al and Si atoms in the lattice, the Al atoms being four-, five- and six-fold coordinated. The xerogel crystallises at 980°C into an alumina-rich mullite and amorphous silica, and the $3Al_2O_3{\cdot}2SiO_2$ stoichiometry is reached at 1300°C by reincorporating the silica in the lattice.

1 Introduction

Due to their excellent high-temperature properties, mullite, $3Al_2O_3{\cdot}2SiO_2$, and mullite-matrix composites have received much attention during the last decade.[1,2] The chemical synthesis of mullite has been exemplary.[3] It is well known that single phase precursors crystallize into mullite at ~980°C while for diphasic precursors this crystallization is delayed to higher temperatures (~1250°C) through transient alumina phases. The synthesis of single phase aluminosilicate gels has been generally performed by organic processes, using all alkoxides or silicon alkoxide (TEOS) and aluminium nitrate. Aqueous processes, starting with colloids or salts, lead usually to diphasic gels. However chemically homogeneous mullite precursors may also be obtained by aqueous routes. The precursor solution may be conveniently prepared by hydrolysing tetraethoxysilane (TEOS) in a solution of aluminium nitrate. This precursor solution, of aluminium nitrate and silicic acid, may be transformed into chemically homogeneous amorphous materials by an organic gel-assisted process,[4] by spray-drying[5] or by rapid precipitation into an alcoholic solution of a base.[6] While by the addition of a base to hydrolyse the aluminium salt a diphasic precursor is generally obtained, here we present the synthesis of a chemically very homogeneous gel precursor of mullite, by the slow *in situ* generation of ammonia, using urea as the base generator. ^{27}Al and ^{29}Si NMR spectroscopy has been used to study the different steps of the synthesis, from the solution to the ceramic.

2 Experimental

2.1 Synthesis

Tetraethoxysilane (TEOS), $Si(OC_2H_5)_4$ (Merck), was added in the stoichiometric ratio to a stirred 0·6 M aqueous solution of aluminium nitrate nonahydrate (Aldrich). By hydrolysis of TEOS a clear solution was obtained. Urea $CO(NH_2)_2$ (Merck) was added (1·8 urea mole per aluminium nitrate mole) and the solution was stored at 80°C. A gel was obtained after a few hours, a clear sol after 3 days, and a second gel after a week. This gel was filtered, washed with water, dried at 100°C, and further calcined to different temperatures. Preparations were also made by adding various quantities of urea to the precursor solution, and storing at 80°C for 20 days or 100°C for 7–10 days. These preparations corresponded to different degrees of partial hydrolysis of the aluminium cations. For some preparations gadolinium was added from nitrate as a paramagnetic relaxation agent for the ^{29}Si NMR spectroscopy study (0·04 wt% Gd_2O_3 in the final oxide).

2.2 Characterisation

NMR experiments were recorded on a Bruker MSL 300 spectrometer operating at a magnetic field of 7·04 Tesla. For ^{27}Al a pulse length of 0·6 μs and a recycle time of 1 s were used, and for ^{29}Si a pulse length of 2 μs and a recycle time of 10 s. High resolution solid state MAS-NMR spectra were obtained in zirconia rotors spinning the samples at the magic angle (54°44') at 15 kHz and 4 kHz respectively for Al and Si. The chemical shifts are given with respect to tetramethylsilane and $[Al(H_2O_6]^{3+}$ in aqueous aluminium nitrate. The isotropic chemical shift positions (δiso) and the estimated minimum quadrupolar frequencies (ν_Q) are measured using central and satellite transitions as proposed by Jäger[7] and Massiot *et al.*[8]

3 Results and Discussion

When TEOS is added to an acidic solution of aluminium nitrate (pH ~ 2) it is hydrolysed into silicic acid. At this pH the rate of hydrolysis is maximum while that of polycondensation of silicic acid is minimum.[9] If no base is added to this solution the silicic acid will slowly polymerise into silica gel, after several weeks at room temperature or a few days at 100°C. This silica gel may be filtered and carefully washed and dried. By analysis of the gel and the filtrate it is shown that no reaction occurs between the silicated and aluminated species.

Urea has been used as a base generator in the preparation of oxide ceramics.[10,11] At temperatures higher than 60°C, urea is hydrolysed in aqueous solutions:[12]

$$CO(NH_2)_2 + 3\ H_2O \rightarrow CO_2 + 2\ NH_4OH$$

For the solution of aluminium nitrate and silicic acid the slow *in situ* generation of ammonia will hydrolyse and polycondense the aluminium species while increasing the pH will result in polycondensation of the silicic acid, although the raising of the pH is significant only at the end of the hydrolysis of the aluminium nitrate. A copolycondensation, or at least a good level of mixing of aluminate and silicate species may be expected by this reaction. In fact the reaction proceeds by a very different way. When 1·8 mole of urea per mole of aluminium nitrate are added to the solution, that is in slight excess for the complete hydrolysis of aluminium (which would require 1·5 mole of urea), at 80°C a gel is formed within a few hours. Then this gel is slowly desegregated and a clear colloidal sol is obtained after 3 days and a second gel after a week. For the study of the reactions occurring during the synthesis, a series of preparations were made with precise quantities of urea corresponding to partial hydrolyses of aluminium. By storing at 80°C for 20 days or at 100°C for 7–10 days it was considered that practically all the urea had reacted. Even by ageing at 100°C for much longer times the obtained gels or sols did not apparently evolve. In these conditions gels were obtained for degrees of hydrolysis h = OH/Al < 0·7, clear sols for 0·8 < h < 2·7 and gels for h > 2·8.

3.1 First gels (h < 0·7)

The chemical compositions in silicon and aluminium for the first gels and the sols are given in Table 1, determined by EDX analysis on the gels filtered and carefully washed and dried, and on the freeze-dried materials obtained from the concentrated and dialysed sols. The first gel which is formed is probably a pure silica gel; as aluminium is hydrolysed it reacts with this silica gel and is responsible for its digestion to small particles of aluminosilicate species.

The ^{29}Si MAS NMR spectra confirm the nature of the first gels (Fig. 1). For h = 0·1 the spectrum is characteristic of polymerised silica with main resonances at −110 ppm (Q^4) and −102 ppm (Q^3). In this Q^n notation,[13] Q represents a silicon atom in a SiO_4 tetrahedron and n indicates the number of other Q units attached to it. Q^4 denotes three-dimensionally cross-linked tetrahedra, that is fully polymerised silica, and Q^3 chain-branching sites. As the hydrolysis progresses we note a shift of the resonance bands to lower fields. The intensity of the band at −110 ppm decreases and other bands appear at −90 and −78 ppm. Two different phenomena may contribute to this shifting of the resonance lines: the depolymerisation of the silica network and the replacement of silicon by aluminium in the second sphere of coordination of the silicon atoms. Each depolymerisation step (breaking of Si–O–Si to Si–O–OH) results in a shift of ca 10 ppm, while for each replacement of Si–O–Si bonds by Si–O–Al bonds a chemical shift

Table 1. Evolution of the Al/Si ratio in the gels and the colloids with the degree of hydrolysis h of aluminium nitrate

h = OH/Al	0·2	0·4	0·6	0·8	1·0	1·2	1·5	1·8	2·0	2·4	2·6
Al/Si	0·11	0·21	0·38	0·67	0·82	1·1	1·3	1·7	1·95	2·2	2·55

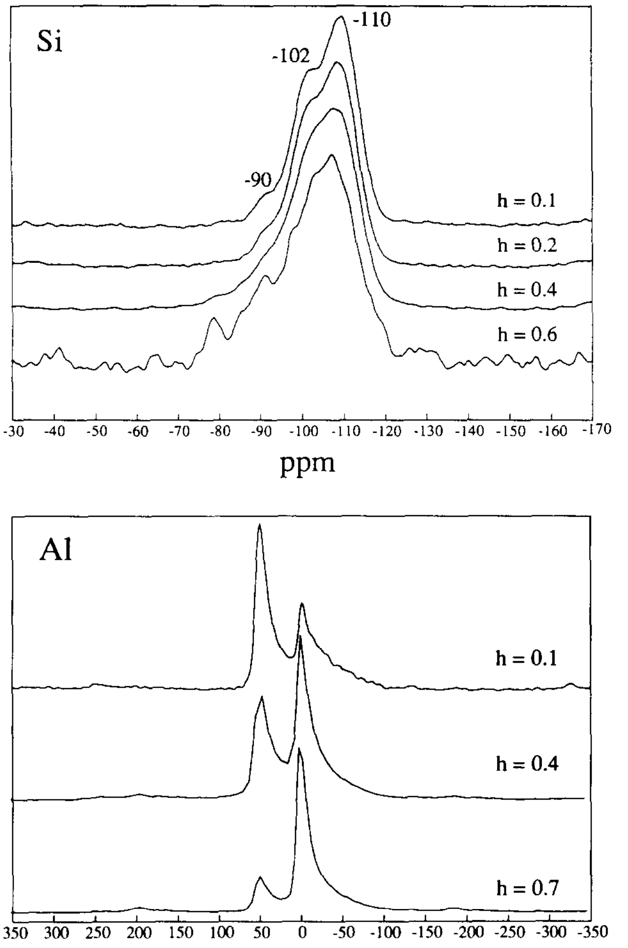

Fig. 1. ^{29}Si and ^{27}Al MAS NMR spectra of the first gels for different degrees of hydrolysis for aluminium.

of ca 5 ppm is expected for the silicon atoms.[13] The two reactions occur during the hydrolysis and further studies are necessary for precise attribution of the new lines appearing on the NMR spectra.

The first aluminium atoms incorporated in the silica gel are mainly tetracoordinated, with the apparent chemical shift at 50 ppm (Fig. 1) for this quadrupolar nucleus, characteristic of AlO$_4$ tetrahedra. Some Al also occurs in hexacoordinated symmetry, at 0 ppm, characteristic of AlO$_6$ octahedra. As the hydrolysis progresses the ratio Al(VI)/Al(IV) increases and the majority of the aluminium atoms incorporated in the gel are hexacoordinated.

Whatever the quantity of urea added to the precursor solution, a silica gel is always formed in the first step of the reaction. Urea acts as a catalyst in the polycondensation of silicic acid in the presence of aluminium nitrate. The incorporation of the first aluminium atoms in tetrahedral symmetry is in agreement with other reports on silica-rich single phase aluminosilicate gels.[14] When the content in alumina increased the ratio Al(VI)/Al(IV) also increased.[15]

3.2 Colloidal sols (0·8 < h < 2·7)

The ^{29}Si and ^{27}Al NMR spectra of the colloidal sols (Fig. 2) show an evolution of the environments for the silicon atoms. For the ^{29}Si NMR spectroscopy the colloidal sols have been greatly concentrated but remained optically clear. The remaining resonance bands at –110 and –102 ppm, predominant in the first gel progressively disappear and are replaced by lines at –90 and –85 ppm. These lines then disappear in their turn and the evolution is towards a single resonance at –78 ppm for a degree of hydrolysis h slightly higher than 2·4.

The static ^{27}Al NMR spectra show only a band at 0 ppm corresponding to hexacoordinated aluminium atoms, including the non hydrolysed aluminium cations [Al(H$_2$O)$_6$]$^{3+}$. But due to molecular-weight broadening effects associated with the quadrupolar aluminium nucleus in highly distorted symmetry, many Al species may be not observable by NMR spectroscopy under static conditions.

The size of the colloidal particles has been determined by dynamic light scattering.[16] For a series of colloidal samples aged at 100°C for 10

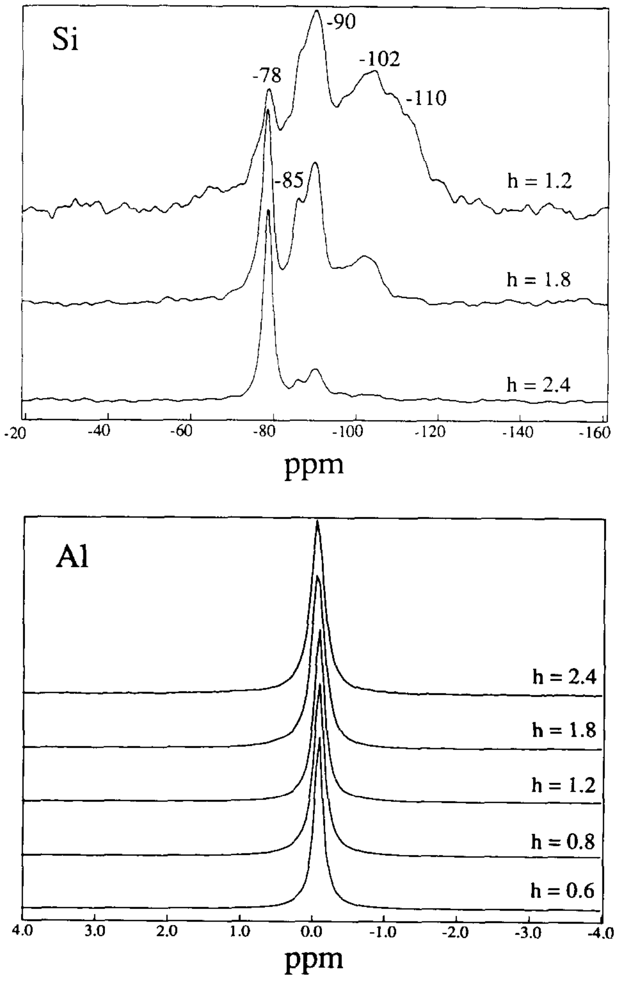

Fig. 2. ^{29}Si and ^{27}Al NMR spectra of concentrated colloidal sols (Si) and colloidal sols (Al) corresponding to different degrees of hydrolysis h for aluminium.

days, the Stokes radius decreases rapidly to values close to 2 nm. A minimum of 1·64 nm is observed around h = 2·6, with a narrow size distribution (+ 0·03 nm). For higher h values the size of the particles increases sharply just before the second gelation.

3.3 The second gel (h > 2·8)

For degrees of hydrolysis higher than 2·8 another gel is obtained, resulting from the cross linking of the colloidal particles by the condensation of the last aluminium atoms being hydrolysed. By further ageing syneresis occurs with cracking of the gel. The gel is filtered and washed to eliminate the ammonium nitrate formed during the hydrolysis and dried. Since no aluminium or silicon were found in the filtrate, this gel is an aluminosilicate gel precursor of stoichiometric 3 : 2 mullite.

The ^{29}Si and ^{27}Al MAS NMR spectra (Fig. 3) show for silicon atoms a sharp resonance at –78 ppm as in the colloidal sols for high degrees of hydrolysis, and for aluminium atoms practically a single hexacoordinated symmetry at ~0 ppm. There remains however some tetrahedrally coordinated atoms (at ~50 ppm) not visible in static conditions in the colloidal samples, even though probably present. These local environments for silicon and aluminium atoms are very similar to those in natural imogolite.[17-19] In this tubular mineral each silicon atom is linked to three hexacoordinated aluminium atoms via oxo bridges and to one hydroxyl group, and the NMR spectrum exhibits a unique resonance band at ~–78 ppm; and all the aluminium atoms are hexacoordinated. The high degree of similarity in the local structure and the sharpness of resonance bands indicate a very high degree of chemical homogeneity in the colloidal samples before the gelation and in the gel. However the particle size of the colloidal species before gelation, substantially too low for a tubular morphology, and the chemical composition (Al/Si = 2·5–3) are more related to allophane than imogolite. While in imogolite the Al/Si atomic ratio is about 2, for allophanes, very poorly crystalline hydrous aluminosilicates with a hollow spheroidal structure, a much wider range of composition is available.[20-22] Allophanes usually also possess imogolite-like orthosilicate units giving rise to a sharp resonance at ~–78 ppm.[22]

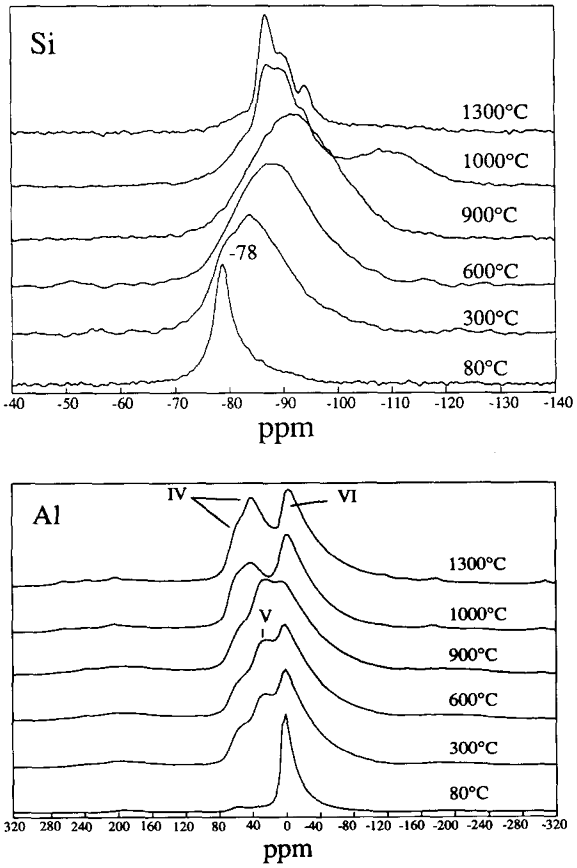

Fig. 3. ^{29}Si and ^{27}Al MAS NMR spectra of the mullite precursor gel to the ceramic after heat treatment for 1 h at different temperatures.

3.4 Structural evolution with heat-treatment

Heated at 10°C/min the second gel (h = 3) exhibits only a single and strong exotherm at 980°C, on differential scanning calorimetry. By X-ray diffraction this thermal event is checked to be the crystallization into mullite. For the NMR spectroscopy study samples were calcined for 1 h at different temperatures (Fig. 3). There is a strong modification in the local environments of the cations at low temperature treatment, between 100 and 300°C. At 300°C the site distribution for the silicon atoms is much broader than at 100°C, with a shift to higher fields which may result from the condensation of hydroxyl groups. This broad line indicates a random distribution of Si and Al atoms in the lattice. For the aluminium atoms tetrahedral (δiso = 70-72 ppm) and 'pentahedral' (δiso = 41 ppm) coordinations appear. So the imogolite-like local structure is rapidly lost by heat-treatment. This behaviour is also more characteristic of allophane than imogolite. In imogolite the sharp resonance is still the major band at 400°C (15 min) while in allophane it disappears at about 200°C.[19,22]

With increasing temperature above 300°C, the structural evolution of this precursor becomes more similar to those of other single phase aluminosilicate gel precursors of mullite.[23-26] There is a regular shift of the maximum of the broad resonance for the silicon atoms until 900°C. For the aluminium atoms, the Al(IV) and Al(V) signals increase and are at their apparent maximum intensities at 900°C, before the crystallization temperature.

At 1000°C the sample is crystallised and the environments of the atoms are modified. The 'pentacoordinated' aluminium atoms have disappeared and there are now three Al sites in mullite: one octahedral (δiso = 10 ppm) and two tetrahedral, assignated by Merwin and Schneider[27,28] to T and T* sites of the mullite structure,[29] at 70 and 41 ppm respectively for the isotropic positions. T* refers to tricluster distorted Al tetrahedra, explaining the low chemical shift for Al(IV), at a similar isotropic position to the 'pentacoordinated' atoms in the amorphous state. For silicon atoms the broad signal at −90 ppm is replaced by the characteristic resonances of mullite at −86, −90, −94 and −80 ppm, and a broad signal at −110 ppm, characteristic of silica. This reflects the segregation occurring during the crystallization. The crystallised mullite is richer in alumina and a part of silica is expelled from the lattice.

On further heating, to 1300°C, the free amorphous silica has re-entered the mullite structure and the signal at −110 ppm has disappeared. The material is orthorhombic 3:2 mullite.[28–30] The main resonance at −86 ppm corresponds to Si atoms in a sillimanite-type (Al_2SiO_5) arrangement, while the lines at −90 and −94 ppm reflect a mullite-type Al/Si ordering. The change in the mullite composition from 1000 to 1300°C is accompanied by an apparent increase of the Al(IV)/Al (VI) ratio.

4 Conclusion

This synthesis of mullite precursor proceeds through unexpected reactions. It is shown that a silica gel may be digested by partially hydrolysed aluminium species homogeneously generated inside its network. This leads to aluminosilicate colloids and gels with aluminium and silicon atoms environments close to those in imogolite or allophane. This local arrangement is thermodynamically lost by thermal treatment but a very high degree of mixing of aluminium and silicon atoms is preserved in the amorphous state, and the xerogel crystallises into mullite at low temperature. This synthesis, with the use of urea as a base generator, is well suited to all compositions single phase aluminosilicate gels and especially to mullite precursors.

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References

1. Ceramic Transactions. Vol 6. In *Mullite and Mullite Matrix Composites*, eds S. Somiya, R. F. Davies & J. A. Pask, American Ceramic Society, Westerville, OH, 1990.
2. Proceedings of the Symposium Mullite Processing, Structure and Properties, 43rd Pacific Coast Regional Meeting, The American Ceramic Society, *J. Am. Ceram. Soc.*, **74**(10) (1990).
3. Sacks, M. D., Lee, H. W. & Pask J. A., A review of powder preparation methods and densification procedures for fabricating high density mullite. In ref. 1, pp. 167–207.
4. Douy, A., Organic gels in the preparation of silicate powders. 1. Mullite. *J. Eur. Ceram. Soc.*, **7** (1991) 117–23.
5. Jaymes, I. & Douy, A., Homogeneous mullite-forming powders by spray drying aqueous solutions. *J. Am. Ceram. Soc.*, **75** (1992) 3154–6.
6. Jaymes, I. & Douy, A., Homogeneous precipitation of mullite precursors. *J. Sol-Gel Sci. & Technol.*, **4** (1995) 7–13.
7. Jäger, C., How to get more from ^{27}Al MAS NMR by high speed satellite transition spectroscopy. *J. Magn. Reson.*, **99** (1992) 353–62.
8. Massiot, D., Coté, B., Taulelle, F. & Coutures, J. P., ^{27}Al MAS NMR of crystalline and amorphous materials. In *Applications of NMR to Cement Sciences*, eds P. Colombet & A. R. Grimmer, Gordon and Breach, New York, 1994, pp. 153–69.
9. Iler, P. K., *The Chemistry of Silica*, Wiley, New York, 1979.
10. Kato, A., Inoue, K. & Katatae, Y., Sintering behavior of yttria-stabilized zirconia (YSZ) powder prepared by homogeneous precipitation. *Mat. Res. Bull.*, **22** (1987) 1275–81.
11. Wood, T. E., Siedle, A. R., Hill, J. R., Skarjune, R. P. & Goodbrake, C. J., Hydrolysis of aluminum. Are all gels created equal? *Mat. Res. Symp. Proc.*, **180** (1990) 97–116.
12. Shaw, W. H. R. & Bordeaux, J. J., The decomposition of urea in aqueous media. *J. Am. Chem. Soc.*, **77** (1955) 4729–33.
13. Engelhardt, G. & Mitchell, D., *High Resolution Solid State NMR of Silicates and Zeolites*, Wiley, New York, 1987.
14. Irwin, A. D., Holmgren, J. S. & Jonas, J., ^{27}Al and ^{29}Si NMR study of sol–gel derived aluminosilicates and sodium aluminosilicates. *J. Mat. Sci.*, **23** (1988) 2908–12.
15. Komarneni, S., Roy. R., Fyfe, C. A., Kennedy G. J. & Strobl, H., Solid state ^{27}Al and ^{29}Si magic angle spinning NMR of aluminosilicate gels. *J. Am. Ceram. Soc.*, **69**, (1986) C-42–4.
16. Jaymes, I., Douy, A., Massiot, D. & Busnel, J. P., to be published.
17. Barron, P. F., Wilson, M. A., Campbell, A. S. & Frost, R. L., Detection of imogolite in soils using ^{29}Si NMR. *Nature*, **299** (1982) 616–18.
18. Goodman, B. A., Russel, J. D., Montez, B., Oldfield E. & Kirkpatrick, R. J., Structural studies of imogolite and allophanes by aluminum-27 and silicon-29 nuclear magnetic resonance spectroscopy. *Phys. Chem. Mineral.*, **12** (1985) 342–6.
19. MacKenzie, K. J. D., Bowden, M. E., Brown, I. V. M. & Meinhold, R. H., Structure and thermal transformations of imgolite studied by ^{29}Si and ^{27}Al high-resolution solid-state nuclear magnetic resonance. *Clays & Clay Minerals*, **37** (1989) 317–24.
20. Farmer, V. C., Adams, M. J., Fraser, A. R. & Palmieri, F., Synthetic imogolite: properties, synthesis and possible applications. *Clay Miner.*, **18** (1983) 459–72.
21. Wada, S. I., Eto, A. & Wada, K., Synthetic allophane and imogolite. *J. Soil Sci.*, **30** (1979) 347–55.
22. MacKenzie, K. J. D., Bowden, M. E. & Meinhold, R. H., The structure and thermal transformations of allophanes studied by ^{29}Si and ^{27}Al high-resolution solid-state nuclear magnetic resonance. *Clays & Clay Minerals*, **39** (1991) 337–46.
23. Sanz, J., Sobrados, I., Cavalieri, A. L., Pena, P., de Aza, S. & Moya, J. S., Structural changes induced on mullite

precursors by thermal treatment: a ^{27}Al MAS NMR investigation. *J. Am. Ceram. Soc.*, **74** (1991) 2398–403.

24. Yoldas, B. E., Effect of ultrastructure on crystallization of mullite. *J. Mat. Sci.*, **27** (1992) 6667–72.
25. Selvaraj, U., Komarneni, S. & Roy, R., Structural differences in mullite xerogels from different precursors characterized by ^{27}Al and ^{29}Si MAS NMR. *J. Solid State Chem.*, **106** (1993) 73–82.
26. Jaymes, I., Douy, A., Florian, P., Massiot, D. & Coutures, J. P., New synthesis of mullite. Structural evolution study by ^{17}O, ^{27}Al and ^{29}Si MAS NMR spectroscopy. *J. Sol-Gel Sci. & Technol.*, **4** (1995) 7–13.
27. Merwin, L. H., Sebald, A., Rager, H. & Schneider, H., ^{29}Si and ^{27}Al MAS NMR spectroscopy of mullite. *Phys. Chem. Miner.*, **18** (1991) 47–52.
28. Schneider, H., Merwin, L. & Sebald, A., Mullite formation from non-crystalline precursors. *J. Mat. Sci.*, **27** (1992) 805–12.
29. Angel, R. J. & Previt, C. T., Crystal structure of mullite: a reexamination of the average structure. *Am. Mineral.*, **71** (1986) 1476–82.
30. Ban, T. & Okada, K., Analysis of local cation arrangement in mullite using ^{29}Si MAS NMR spectra. *J. Am. Ceram. Soc.*, **76** (1993) 291–6.