Structural Investigation and Energetics of Mullite Formation from Sol–Gel Precursors

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The influence of homogeneity of sol–gel precursors on mullite ($Al_6Si_2O_{13}$) formation was examined with a combination of structural and thermodynamic characterization by NMR, X-ray diffraction, and drop solution calorimetry. The most homogeneous gels crystallize to mullite at 980 °C. Gels with distinct silica and alumina phases crystallize to mullite above 1250 °C. Crystallization at 980 °C and the nature of the dominant crystalline phase, spinel or mullite, were related to the abundance of pentacoordinated aluminum atoms in the amorphous phase at 900 °C. The enthalpy of crystallization to mullite from the gels varies from −112 kJ/mol($Al_6Si_2O_{13}$) for complete mullite formation at 980 °C from a homogeneous gel formed by controlled hydrolysis of TEOS and aluminum isopropoxide, to −33 kJ/mol for mullitization at 1250 °C from a heterogeneous gel made of boehmite in hydrolyzed TEOS. Gels with intermediate mixing formed an alumina-rich spinel phase at 980 °C, which contained 7 wt % SiO_2 as shown by ^{29}Si MAS NMR. Mullite formed at 980 °C is aluminum-rich with an Al/Si ratio of 5, with the excess silica phase separating as amorphous silica. Between 950 and 1200 °C the silica and mullite react increasing the silicon content in mullite crystals. The enthalpy of the substitution reaction, $Al^{3+} + {}^1/_2\,\text{vacancy} \rightarrow Si^{4+} + {}^1/_2O^{2-}$, was determined to be −52 kJ/mol. The enthalpy of formation of mullite from mixtures of α-alumina and quartz varied with the Al/Si ratio and was a minimum at Al/Si = 3.2.

Introduction

Mullite ($3Al_2O_3{\cdot}2SiO_2$) is the only stable phase in the Al_2O_3–SiO_2 binary system. The excellent high-temperature properties of mullite make it an attractive ceramic material for high-temperature mechanical applications.[1] Mullite is attractive due to its high creep resistance,[2,3] its low thermal expansion,[4] and its outstanding chemical stability. Despite extensive study,[5–22] the formation process of mullite remains controversial. There are disagreements over the silica–alumina phase diagram and the equilibrium solid solution limits of mullite around the composition Al/Si = 3.[23–28] Many studies examined the exothermic reaction at 980 °C, which produces mullite or a spinel phase from kaolinite or silica–alumina gels. The spinel phase was reported to be either γ-alumina or an aluminosilicate spinel. The exotherm at 980 °C and the preference for mullite or spinel are related to the degree of homogeneity in the precursor. Mullitization is easier with more intimate mixing between Al and Si polyhedra in the precursor.

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Three mullite crystallization paths from synthetic precursors of mullite stoichiometry have been reported in the literature, differentiated by differential thermal analysis (DTA) heating curves and X-ray diffraction. The DTA curve of type 1 exhibits a single sharp exothermic peak at about 980 °C. The DTA curve of type 2 consists of two exotherms: one at about 980 °C and a broader one around 1250 °C. The DTA curve of type 3 consists of one unique exotherm at high temperature, around 1300 °C. The X ray diffraction patterns for type 1 and 2 show an amorphous to crystalline transition at 980 °C; type 1 forms mullite and type 2 shows formation of both mullite and a spinel phase. When a spinel phase is present, a second exotherm is observed around 1250 °C, which leads to the complete transformation into orthorhombic mullite. Type 3 materials have already crystallized to a transitional alumina before the exotherm observed at about 1300 °C. After that exothermic peak, only mullite is detected.

Direct mullitization at 980 °C occurs when fully homogeneous precursors are prepared from salts (aluminum nitrate) or alkoxides (tetraethoxysilane, aluminum isopropoxide). In the literature, type 1 gels are often called single-phase precursors, implying that silicon and aluminum atoms are mixed on an atomic scale. Type 1 gels are obtained by spray pyrolysis,[29] by slow hydrolysis of initial compounds[8] or by prehydrolysis of either the Si or the Al alkoxide followed by addition of the other unhydrolyzed alkoxide.[15] The route of type 2, which leads to the formation of a transitory spinel phase, is generally obtained with the same initial compounds (salts or alkoxides); however the gel is most frequently obtained by rapid hydrolysis[30] of the initial compounds. Type 3 precursors show silica- and alumina-separated phases. The precursors are called colloidal gels or diphasic gels and the initial compounds are generally silica or a silicon alkoxide and either boehmite (γ-AlOOH)[12,7] or bayerite ($Al(OH)_3$).[31]

The DTA exotherm at 980 °C has been controversial; it has been attributed to crystallization of mullite or spinel or both. Why should the formation of different crystalline structures occur at the same temperature? In 1991, ^{27}Al MAS NMR studies[32] showed that the exothermic and expansive effects observed at 980 °C were associated with aluminum atom rearrangement; it was observed that five-coordinated aluminum atoms present in the amorphous materials disappear above 980 °C. The transformation of metastable five-coordinated aluminum sites into more stable environments could be the origin of the exotherm which causes the crystallization of the two phases, mullite and spinel, at the same temperature.

The three routes for mullite formation previously described indicate that the degree of homogeneity of aluminum and silicon polyhedra is critical in determining the crystallization path.[20] It is difficult to estimate the scale of mixing of aluminum and silicon in the amorphous structures. Recently, Taylor[33] studied mullitization from polymeric precursors; he defined a degree of homogeneity, Pm/Ps, as the mullite/spinel ratio at 980 °C. He showed that Pm/Ps increases with the amount of five-coordinated aluminum atoms present in the aluminosilicate xerogel.

The transitory spinel phase that appears in route of type 2 after the 980 °C exothermic peak has a poorly defined X-ray diffraction pattern which exhibits broad peaks very similar to those of γ-alumina. Because of the broad peaks, it is difficult to identify the spinel phase as γ-alumina or an aluminosilicate phase (a solid solution between γ-alumina and silica). In the past three decades, the spinel phase was characterized using chemical and/or structural studies. In 1959, Brindley and Nakahira[5] proposed the composition of the spinel-type phase formed from metakaolin was $2Al_2O_3{\cdot}3SiO_2$. In 1978, on the basis of leaching experiments, Chakravorty et al.[11] claimed that the spinel phase had the same composition as $3Al_2O_3{\cdot}2SiO_2$ mullite, and so they designated this transitory phase as the cubic form of mullite. On the basis of analytical TEM examination, Aksay[34] proposed that the spinel phase was an aluminosilicate γ-type structure about 8 wt % in SiO_2. Using ^{29}Si and ^{27}Al NMR, Brown et al.[35] in 1985 found that the NMR evidence was more consistent with pure γ-alumina than with an Al–Si spinel. Okada[8] in 1986 carried out an analytical TEM study of fired and NaOH-treated specimens and found a composition around 8 wt % of SiO_2, in agreement with Aksay's results. Finally, in 1989, Low[19] claimed that the Al–Si spinel was similar to (2:1) mullite, i.e., $SiAl_4O_8$. Thus, despite extensive investigation, the spinel composition is still a subject of debate.

The structure and composition of mullite are variable. The composition of mullite has often been deduced in the literature from the measurement of unit cell parameters. Cameron[36] found a linear relation between the length of the *a* axis and mullite composition. Mullites formed at about 980 °C from either synthetic precursors or kaolinite were rich in alumina. A progressive contraction of the mullite *a* parameters with increasing temperature was generally observed,[5,30,35] indicating that the mullite composition decreased from 71 to 60 mol % Al_2O_3. TEM[10] studies found that mullite formed at 950 °C was 66 mol % Al_2O_3, and the mullite composition gradually approached the bulk composition $3Al_2O_3{\cdot}2SiO_2$ with increasing temperature to 1400 °C. It is believed that the substitution reaction

$$Si^{4+} + {}^{1}/_{4}O^{2-} \leftrightarrow Al^{3+} + {}^{1}/_{2}\,\text{vacancy}$$

is responsible for the existence of the mullite solid solution in the range of composition $2.6 \le Al/Si \le 6.3$.[36,37] Si^{4+} ions are substituted by Al^{3+} ions in tetrahedral chains where Al and Si atoms alternate, while tetrahedra-linking oxygen atoms O_c are removed. Edge-shared AlO_6 octahedra remain unchanged. Cameron[37] expressed the solid solution of mullite by the formula $Al^{VI}_2[Al^{IV}_{2+2z}Si^{IV}_{2-2z}]O_{10-z}$, where *z* is the number of O_c atoms missing per unit cell.

The purpose of our study was to combine local structural characterizations and calorimetric experiments to examine different mullite crystallization paths. Three different precursors with a composition corresponding to Al/Si = 3, were prepared by sol–gel techniques with different degrees of mixing to investigate the influence of homo-

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geneity on the evolution of the local atomic environment and the energetics of mullite formation.

^{29}Si and ^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR) was employed to follow the evolution of the local environments of aluminum and silicon atoms from the precursor to the crystalline material. X-ray diffraction (XRD) was used to study long-range order. The enthalpy of structure transformations was examined using high-temperature drop solution calorimetry in molten lead borate at 703 °C.

Our results confirm the importance of the aluminum site distributions, especially the presence of five-coordinated aluminum environments in the amorphous phase at 900 °C, to obtain low-temperature mullitization. NMR determined the silica content of the spinel phase. Finally, drop solution calorimetry leads to the determination of the enthalpy differences associated with structural transformations during the different crystallization processes; it is also shown that the relative stability of mullite samples prepared from different routes can be correlated to the mullite chemical composition.

Experimental Procedure

Preparation Methods. The starting materials were tetraethoxysilane (TEOS, 99% purity, Aldrich Chemical) and either aluminum isopropoxide (AiP, 98% purity, Aldrich Chemical) or boehmite, γ-AlOOH (Catapal alumina, Vista Chemical). The large difference in hydrolysis rates between aluminum and silicon alkoxides was exploited to prepare two precursors M1 and M2 with different degrees of mixing of Al and Si polyhedra. To ensure a high degree of homogeneity of silicon and aluminum polyhedra in precursors M1, TEOS was partially prehydrolyzed in aqueous acid. AiP was added to this sol, and the hydrolysis was completed. In precursor M2, TEOS and AiP were mixed in 2-propanol at 60 °C and then hydrolyzed simultaneously by the addition of water. In precursor M3, TEOS was directly added to an aqueous colloidal dispersion of boehmite and the sol was then stirred for 1 day, before it was dried. The precursors were synthesized in a way so that the degree of homogeneity of aluminum and silicon atoms decreases from M1 to M3.

Precursor M1: TEOS (12.50 g) was dissolved in absolute ethanol (270 g) at room temperature and 1.62 g of a nitric acid solution at pH = 1 was added to prehydrolyze the TEOS; the prehydrolysis H_2O/TEOS molar ratio was 1.5. After 4 h of mixing, AiP powder (36.76 g) was directly added, and the mixture was vigorously stirred for 24 h. Hydrolysis was completed by addition of a mixture of water and ethanol (10 wt % of water: 15.9 g of H_2O + 144.1 g of ethanol). The number of moles of water was $n_{H_2O} = 2.5(2n_{TEOS} + 1.5n_{AiP})$ where n_{TEOS} and n_{AiP} were the number of moles of TEOS and AiP, respectively. After 24 h of vigorous stirring, the sol was dried in an open beaker overnight at room temperature, followed by drying at 110 °C in an oven for 24 h.

Precursor M2: TEOS (8.33 g) and AiP (24.51 g) were dissolved in 2-propanol (200 g) at a temperature of 60 °C. After 4 h of mixing, the two alkoxides were simultaneously hydrolyzed by mixing with a water in 2-propanol solution (10 wt % of water: 10.8 g of H_2O + 97.2 g of 2-propanol) for 24 h at 60 °C. The amount of water for hydrolysis was such that $n_{H_2O} = 2(2n_{TEOS} + 1.5n_{AiP})$. The sol was dried in an open beaker overnight at 60 °C, then completely dried in a drying oven at 110 °C for 24 h.

Precursor M3: An aqueous colloidal dispersion of boehmite was prepared (pH = 3) with a concentration of 4 wt % in Al_2O_3. TEOS (10.42 g) was directly added to the dispersion (191.25 g) and the mixture was stirred for 24 h. The sol was dried in the same manner as in route M1.

The precursors were ground into powders using an agate mortar and pestle. Each sample was heated at 1 °C/min from room temperature to 800 °C and held at temperature for 6 h and then heated from 800 °C to the desired temperature (from 950 to 1650 °C) at 3 °C/min and held for 6 h. For route M1, the precursor was also annealed for 24 h at 950, 1000, and 1100 °C.

Characterization Methods. *Differential thermal analysis*: The DTA analyses were performed using a Perkin-Elmer differential thermal analyzer 1700, with 0.1-g samples in Pt crucibles. The DTA heating curves were recorded from 800–1400 °C at a heating rate of 10 °C/min in air.

X-ray diffraction analysis: Powder X-ray diffraction measurements were performed using a Scintag PAD-V diffractometer with Cu Kα radiation; DMS 2000 v2.64 software was used to analyze the data. Crystallite sizes were estimated using Scherrer relation. The half-width of the diffraction profile due to the sample was obtained from the measured breadth minus the instrumental breadth estimated with LaB_6 standard. A multiple-line analysis was employed to get more precise results. Silicon was used as an external standard for calibrations for 2θ positions. A step scanning technique of 0.02° in 2θ interval and fixed time of 2–3 s from a 2θ of 15–70° was applied for lattice parameters measurements. A least-squares fit was used to calculate the lattice parameters.

Nuclear magnetic resonance: MAS NMR experiments were done using a JEOL 270 spectrometer operating at 53.7 MHz for ^{29}Si and 70.4 MHz for ^{27}Al. The spinning rate was 4 kHz. A repetition time varying from 60 to 600 s and a radio-frequency pulse angle of about $\pi/6$ were used for ^{29}Si spectra, a repetition time of 1–10 s and a pulse delay of about $\pi/10$ were used for ^{27}Al spectra. Between 250 and 720 accumulations were needed for acquiring ^{29}Si spectra and between 120 and 1200 for ^{27}Al spectra. ^{29}Si NMR spectra were simulated using a least-squares program. $Al(H_2O)_6^{3+}$ and tetramethylsilane were used as external standard references for ^{27}Al and ^{29}Si chemical shifts, respectively.

Calorimetry: A twin calorimeter of the Tian Calvet type was used to measure the enthalpy of drop solution of the samples in molten lead borate ($2PbO–B_2O_3$) solvent. The equipment and general methods of solution calorimetry are described in detail by Navrotsky.[38] Briefly, the calorimeter measures heat flow through a sensitive thermopile which surrounds the sample chamber and separates it from a large alloy block maintained at a constant temperature of 703 °C. The thermopile records a change in voltage corresponding to the small temperature variation occurring during the reaction. The voltage variation is integrated over time. The integrated value is directly proportional to the heat effect. Calibration of the calorimeter is done by the standard Pt drop method.[38]

The sample weights in all experiments varied from 15 to 25 mg. In drop solution calorimetry experiments, samples were dropped from room temperature directly

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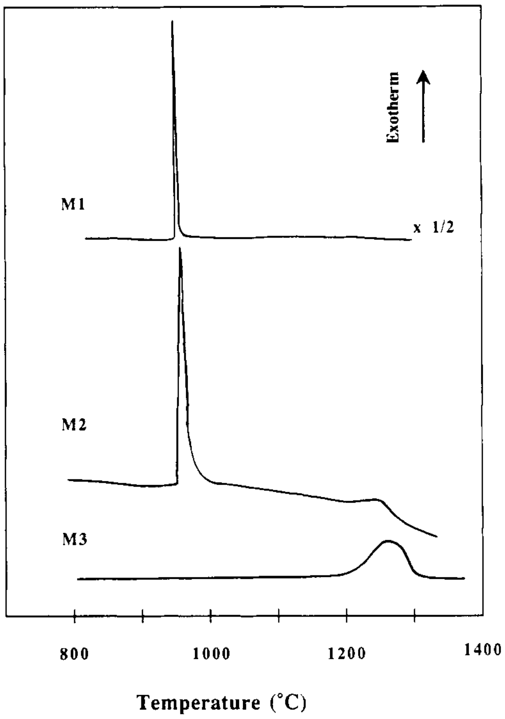

Figure 1. DTA heating curves of materials M1, M2, and M3 previously fired at 800 °C. Heating rate of 10 °C/min in air.

into the solvent (30 g of $2PbO-B_2O_3$) in the calorimeter maintained at 703 °C. The heat of drop solution ΔH_{dsoln} is measured which contains the heat content of the sample ($H°_{703}$–$H°_{25}$) plus the heat of solution ΔH_{soln} of the sample at 703 °C. Since the final states of all the samples (of same composition) after dissolution are the same, the difference in heats of drop solution of two samples gives the enthalpy difference between the initial states. Also, the difference between the sum of heats of drop solution of reactants, and the sum of heats of drop solution of products directly gives the heat of a reaction at room temperature. These calorimetry techniques have been extensively used to measure the metastability, relative to fused silica glass, of silica gels.[39]

Results

Differential Thermal Analysis. The DTA scans of the three precursors annealed at 800 °C for 6 h are shown in Figure 1. The gel M1 exhibited a unique sharp exothermic peak at 982 °C, characteristic of a precursor with a good mixing of Si and Al polyhedra. The precursor M3, prepared from boehmite and TEOS, exhibited an exothermic peak at 1295 °C: this DTA pattern is characteristic of a heterogeneous precursor, usually referred to as a diphasic xerogel. The precursor M2 showed intermediate behavior, with two DTA peaks, at 987 and 1252 °C.

X-ray Diffraction Analyses. *Identification of crystalline phases*: The X-ray diffraction patterns of samples M1, M2, and M3 fired at different temperatures for 6 h are shown in Figure 2a–c, respectively. The patterns characterizing the most homogeneous samples M1 showed the direct crystallization to mullite at 950 °C. A small amount of spinel (γ-type phase), which exhibited an X-ray diffraction pattern similar to γ-alumina (sharp 2θ peak at 43°), was present from 950 to 1100 °C. The XRD patterns of samples M1 annealed for 24 h at 950, 1000, and 1100 °C exhibited only mullite peaks, indicating that the spinel phase transformed to mullite after annealing for 24 h.

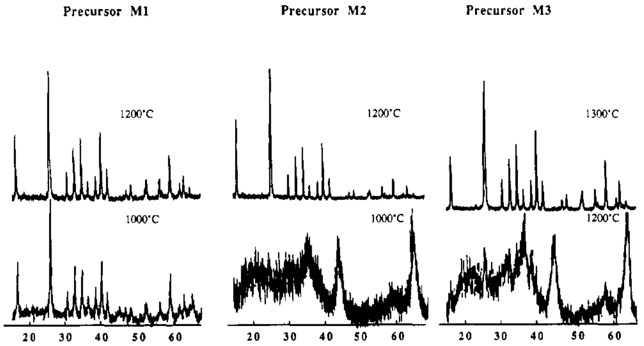

Figure 2. X-ray diffraction patterns of samples (a) M1, (b) M2, and (c) M3 after annealing to the temperature shown for six hours. Below 900 °C samples M1 and M2 were X-ray amorphous. Sample M3 had the same diffraction pattern for annealing temperatures between 800 and 1200 °C.

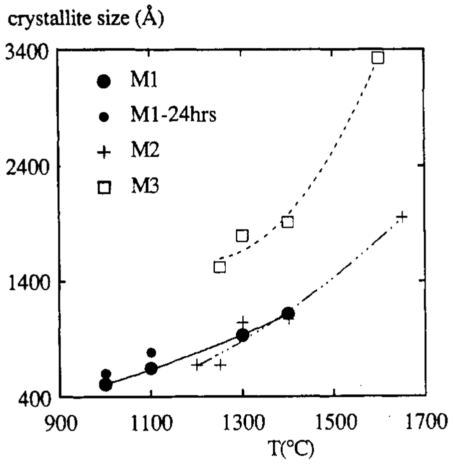

Figure 3. Mullite crystallite sizes in samples M1, M2, and M3 versus annealing temperature. All samples annealed for 6 h at the specified temperature. Crystallite size determination from the half-widths of the diffraction peaks.

The patterns of samples M2 showed the crystallization at 950 °C to a γ-type spinel phase. This poorly crystalline phase was present to 1000 °C. The most intense peak characteristic of mullite ($2\theta = 26.5°$) first appeared at 1100 °C but the main phases at this temperature exhibited patterns characteristic of δ- and θ-type structures. After heating to 1200 °C, only crystalline mullite was observed.

The least homogeneous sample M3 pyrolyzed at 800 °C was weakly crystalline, the X-ray diffraction pattern was similar to γ-alumina. The γ-alumina presumably formed by dehydration of boehmite particles in the gel. Heating to 1100 °C produced a δ-like phase. Upon heating to 1200 °C, some mullite was observed, but the major phases were δ- and θ-like phases. Above 1250 °C, only crystallized mullite is present. Crystalline silica was never observed in the three routes.

Mullite crystallite sizes: Figure 3 presents the mullite crystallite size variation with the annealing temperature. Mullite crystallite sizes in routes M1 and M2 were similar at a given temperature. Crystallite sizes obtained in route M3 were much larger than those in the two other routes. Annealing samples M1 for 24 h at 1000 and 1100 °C led to increased crystallite sizes compared with those after 6-h annealing.

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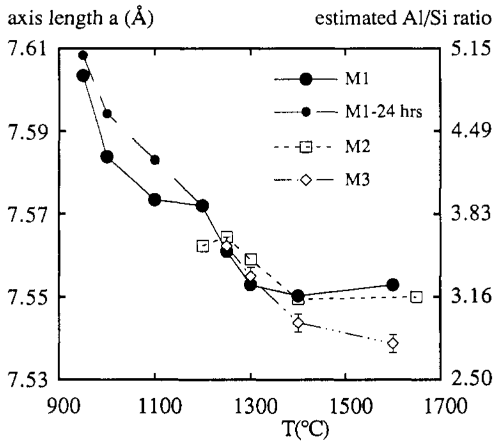

Figure 4. *a* lattice parameter of mullites in samples M1, M2, and M3 versus annealing temperature and estimated Al/Si ratios of mullite crystals. The Al/Si ratios were determined from the lattice parameters using eq 1.

Lattice parameters of the mullite phases: The diffraction patterns of the mullite structures show that all mullite phases have orthorhombic structures, even at temperatures as low as 950 °C in samples M1. Even when splitting of the 210 and 120 lines at $2\theta = 26°$ was not observed (due to too large linewidths), the calculated *a*- and *b*-axis lengths were very different, indicating the absence of any tetragonal phase.

Figure 4 shows the variation of the length of the *a* axis with increasing firing temperature in routes M1, M2, and M3. When samples M1 are fired from 950 to 1200 °C, *a* decreased from 7.61 to 7.57 Å. Samples fired for 24 h at 950, 1000, and 1100 °C had a larger *a* axis than samples fired for 6 h at the same temperatures. Above 1200 °C, the variation in the lattice parameter was small for all the three routes (between 7.56 and 7.54 Å). These observations are in good agreement with results from Okada et al.[30] Above 1400 °C, M3 mullites had smaller *a* lattice parameters than those of M2 and M1.

Compositions of the mullite phases: Cameron[36] showed the existence of a linear relation between the *a*-axis length and the alumina content of mullite phase; a linear relation was also found between the unit cell volume and the alumina content. A least-squares fit to Cameron's data gives the relationship between the lattice parameter, *a* in angstroms, and the mole fraction of alumina in the mullite, $X_{Al_2O_3}$:

$$a = 7.2232 + 0.537X_{Al_2O_3} \quad (1)$$

The lattice parameter and the corresponding Al/Si ratios of mullite crystals in samples M1, M2, and M3 heated at different temperatures determined from eq 1 are shown in Figure 4.

In samples M1, Al/Si of mullite crystals varied from about 4.9 after firing for 6 h at the crystallization temperature, 950 °C, to 3.7 at 1200 °C. Mullites formed at low temperature, 950 °C, were rich in alumina. At this temperature, an amorphous silica-rich phase (observed by ^{29}Si NMR) and a small amount of spinel (observed by X-ray diffraction) coexisted with the mullite. From 950 to 1200 °C, the silica and the spinel phases were incorporated into mullite, and the Al/Si ratio characterizing mullite crystals decreased. In contrast to the decreasing Al/Si ratio with annealing temperature mullite crystals in samples M1 fired for 24 h at 950, 1000, and 1100 °C had higher Al/Si ratios than those of the samples fired for 6 h at the same temperatures. The spinel phase which was present after a firing for 6 h was converted to mullite after 24 h, suggesting that the consumption of spinel leads to the formation of mullite crystals richer in alumina.

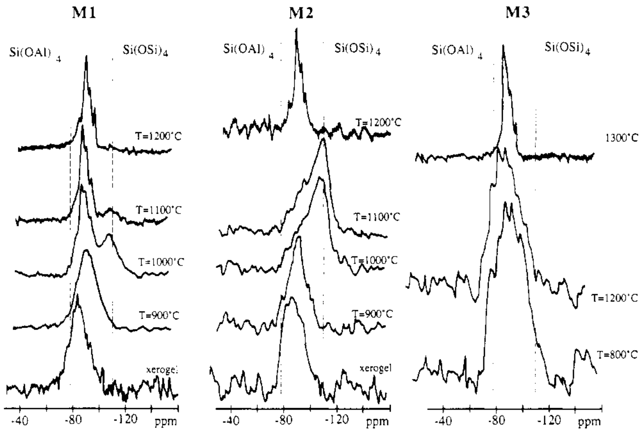

Figure 5. ^{29}Si MAS NMR spectra of samples (a) M1, (b) M2, and (c) M3 heated at various temperatures. Spectrometer operating at 53.7 MHz. Peak shifts are relative to $Si(CH_3)_4$.

The initial mullite crystals formed in routes M1, M2, and M3 had very different compositions: initial mullite crystals had an Al/Si ratio of 4.9 in route M1 (at T = 950 °C) and 3.4 in routes M2 (at T = 1200 °C) and M3 (at T = 1250 °C). Increasing the temperature from 1200 °C to 1600 °C caused the Al/Si ratio of the mullite crystals decrease to about 3, which is the bulk composition. Around 1400 °C, Al/Si ratios were similar in M1 and M2 (Al/Si = 3.2), but different from that in M3 route (Al/Si = 2.9).

Nuclear Magnetic Resonance. *^{29}Si MAS NMR*: Figure 5a–c show the ^{29}Si magic-angle spinning NMR spectra of the precursors and the samples M1, M2, and M3 fired at different temperatures.

Material M1: The spectrum of the precursor showed a broad distribution of silicon sites characteristic of an intimate mixing of aluminum and silicon. Below 900 °C, the ^{29}Si NMR spectra were characteristic of amorphous aluminosilicate structures with a random distribution of silicon and aluminum; the local silicon coordination can be described as $Si(OAl)_n(OSi)_{4-n}$ where n varies between 1 and 4. No detectable silica phase was present below 900 °C. After annealing to between 950 and 1100 °C, the spectra can be analyzed as the sum of a broad peak centered around −110 ppm and a narrower peak centered at −86 ppm with shoulders at −90 and −93 ppm. The feature at −110 ppm may be attributed to a silica-rich phase. The peak at −86 ppm and the shoulders at −90 and −93 ppm correspond to mullite, though the feature was broader than observed for completely crystallized mullite. With increasing temperature to 1200 °C, the features characteristic of mullite get sharper, indicative of more crystalline order. At 1200 °C, the spectrum showed only the mullite peaks at chemical shifts: −85.3, −89.2, and −92.6 ppm. At 1650 °C, the chemical shifts were −86.2, −93.7, and a shoulder at −89 ppm, in good agreement with previous NMR studies of synthesized mullites.[40]

Material M2: The silicon environments in precursor M2, in the gel and after annealing at 800 and 900 °C, were very similar to those of precursor M1. No silica phase was

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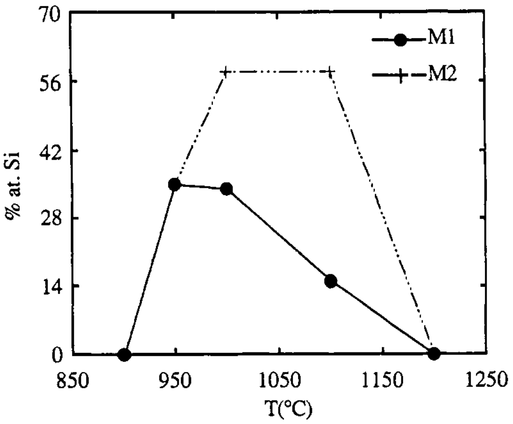

Figure 6. Fractions of silicon atoms present in the amorphous silica-rich phases versus firing temperature.

observed below 900 °C. From 950 to 1100 °C, the predominant signal was centered at −104 ppm, due to an amorphous silica phase. A broad signal centered around −85 ppm was also present which is characteristic of $Si(OAl)_4$ sites present in an alumina-rich aluminosilicate phase. This alumina-rich phase was the spinel phase observed by X-ray diffraction. At 1200 °C, the spectrum abruptly changed to that of well-crystallized mullite; a shoulder at −82 ppm was observed in these samples and vanished above 1400 °C.

Material M3: The spectra of the materials fired at various temperatures from 800 to 1200 °C show a wide distribution of silicon sites characteristic of an aluminosilicate phase containing $Si(OAl)_n(OSi)_{4-n}$ sites with n varying from 0 to 3. The maxima of the spectra was at (−98)−(−100) ppm, indicating the dominant silicon sites corresponded to $n = 1$; $Si(OAl)(OSi)_3$ sites probably exist at the interface between alumina-rich and silica-rich regions. Well-crystallized mullite was observed at 1300 °C.

Estimation of the abundance of the silica-rich phases: The amount of the amorphous silica-rich phase, observed in M1 and M2 from 950 to 1100 °C, was estimated from the deconvolution of the ^{29}Si NMR spectra: the proportion of $Si(OSi)_4$ sites was obtained from the relative area of the signals in the range of chemical shifts: (−104)−(−115) ppm.[41] Figure 6 gives the proportions of silicon sites in the silica-rich phase versus annealing temperature. The maximum amount of silica-rich phase was obtained from 1000 to 1100 °C for sample M2 (58 at. % of the silicon atoms). For the most homogeneous precursor M1, the maximum of 35 at. % was obtained at a firing temperature of 950 °C. The silica-rich phase was gradually consumed and was not detectable after annealing above 1100 °C.

^{27}Al MAS NMR. The ^{27}Al NMR spectra are presented in Figure 7a–c for the materials M1, M2, and M3, respectively. They show the presence of three types of environments: four-, five-, and six-coordinated aluminum sites, which are generally expected in the ranges 50–80, 30–40, and (−10)−(+15) ppm, respectively. It is known that five-coordinated aluminum environments exist in some minerals[42,43] and also in framework aluminosilicate glasses[44] or in amorphous aluminous films.[45] Pentacoordinated aluminum sites were also observed in metakaolinite.[46,47] Well-crystallized orthorhombic mullite (M2 fired at 1600 °C for 4 days) show three ^{27}Al NMR peaks, in good agreement with other authors' observations:[40,48,49] Al^{IV} tetrahedra appear at 60 ppm, Al^{IV*} tetrahedra at 44 ppm, and Al^{VI} octahedra at −3 ppm. Al^{IV*} tetrahedra are present in oxygen triclusters formed by the removal from the structure of oxygen atoms O_c bridging adjacent tetrahedra, this leads to Al^{IV*} sites coordinated by three oxygen atoms.[50,51]

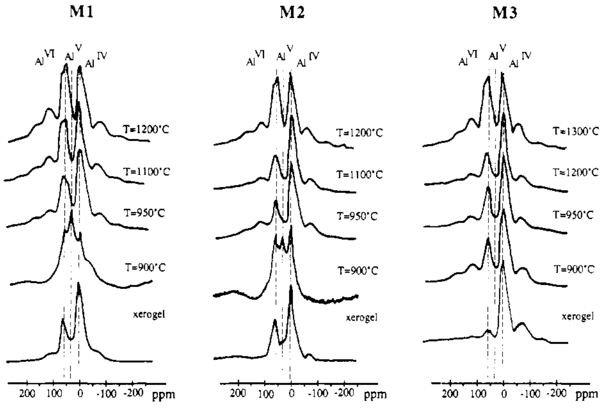

Figure 7. ^{27}Al MAS NMR spectra of samples (a) M1, (b) M2, and (c) M3 heated at various temperatures. Spectrometer operating at 70.4 MHz. Peak shifts are relative to $Al(H_2O)_6^{3+}$.

Material M1: In the precursor, the environments were predominantly Al^{VI} sites (δ = 1.7 ppm) and Al^{IV} sites (δ = 56.8 ppm). A small peak from Al^{V} (δ = 34.3 ppm) was also present. We verified that the weak signal present at 34.3 ppm was not a spinning sideband but was due to pentacoordinated Al sites. Spectra of samples annealed to 900 °C exhibited signals due to the presence of aluminum atoms in coordination states 4, 5, and 6. The five-coordinated environments were predominant in the amorphous phase just before mullite crystallization. Above 950 °C, Al^{V} sites disappeared. From 950 °C, the three types of environments that are characteristic of mullite (Al^{IV},Al^{IV*}, and Al^{IV}) were present but in proportions different from those found in completely crystallized mullite sample. Above 950 °C, the ratios of tetrahedra (four-coordinated) to octahedra (six-coordinated) increased to the value corresponding to well-crystallized mullite at 1200 °C. This evolution coincided with the transformation of the spinel phase to mullite.

Material M2: The gel precursor M2 had a similar distribution of aluminum sites to that of the most homogeneous xerogel M1 (Al^{VI}, Al^{V}, and Al^{IV} signals at 5.2, 35.3, and 60.4 ppm, respectively). In the amorphous phases at 800 and 900 °C, aluminum atoms were present

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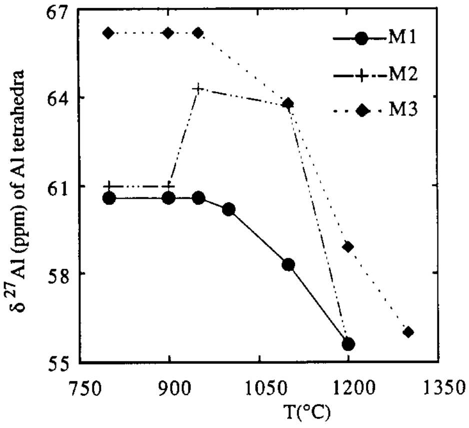

Figure 8. ^{27}Al NMR chemical shifts of Al tetrahedra in samples M1, M2, and M3 versus firing temperature.

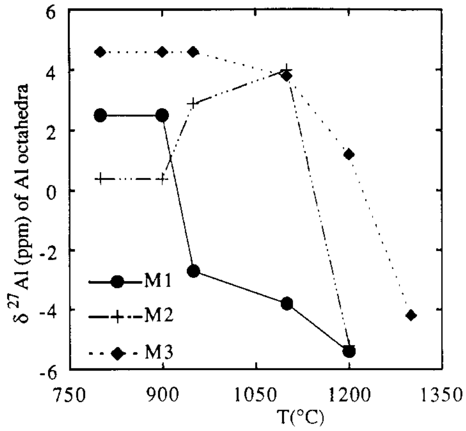

Figure 9. ^{27}Al NMR chemical shifts of Al octahedra in samples M1, M2, and M3 versus firing temperature.

as 4-, 5-, and 6-coordinated sites. Pentacoordinated Al sites were not predominant at 900 °C in this route. Above 950 °C, pentacoordinated aluminum sites did not exist. At 1200 °C, Al^{IV*} sites characteristic of mullite appeared at δ = 41 ppm.

Material M3: The precursor only contained aluminum octahedra present in the boehmite phase. From 800 to 1200 °C, only Al tetrahedra and octahedra were present. The peak due to Al^{IV*} sites appeared (δ = 44 ppm) at 1300 °C, when a spectrum characteristic of crystalline mullite was observed.

Variation of the ^{27}Al NMR chemical shifts: The chemical shifts of Al^{IV} (Figure 8) and Al^{VI} (Figure 9) sites were measured in the three systems M1, M2, and M3 as a function of the annealing temperature. We also measured independently the chemical shifts in reference phases (mullite, γ-, δ-, and θ-aluminas).

Table 1. ΔH_{dsoln} of Boehmite Heated for 6 h at the Indicated Temperatures

T (°C)	phase	ΔH_{dsoln} (kJ/mol of Al_2O_3)
700	γ-alumina	89.1
950	δ-alumina	96.1
1020	θ- and δ-alumina	96.1
1400	α-alumina	108.4

Figure 8 reveals that tetrahedral aluminum environments before any crystallization (at 800 and 900 °C) were similar in systems M1 and M2; the tetrahedral silicon site distributions in amorphous samples M2 and M1 observed by ^{29}Si MAS NMR were also similar. In system M1, the Al^{IV} chemical shift did not change between 900 and 950 °C, indicating that the tetrahedral environments in the amorphous phase were similar to those present in the mullite phase formed at 950 °C. From 950 to 1200 °C, the ^{27}Al chemical shift of Al^{IV} in the M1 system approached that of orthorhombic mullite. The Al^{IV} chemical shift decreased from 60 to 55.6 ppm as the annealing temperature increased from 950 to 1200 °C, consistent with the gradual decrease of Al/Si ratio of mullite crystals.[52]

The Al^{IV} chemical shift for system M2 increased between 900 and 950 °C due to the replacement of silicon atoms by aluminum atoms in the local environment of Al^{IV} atoms, consistent with the segregation in alumina-rich and silica-rich regions. The ^{27}Al chemical shift in system M1 was not sensitive to the segregation, which may be attributed to less silica phase separation in the case of M1 (see Figure 6). Between 1100 and 1200 °C, the sharp decrease of the ^{27}Al chemical shift resulted from mullitization accompanied by a surrounding of aluminum tetrahedra with silicon atoms.

The ^{27}Al chemical shift for the Al^{IV} species, in M3 from 800 to 950 °C, was similar to that of γ-alumina (66 ppm). Between 950 and 1200 °C, the chemical shift decreased. At 1100 °C M2 and M3 had similar Al^{IV} chemical shifts. Complete atomic mixing of Al and Si tetrahedra due to mullitization occurred between 1200 and 1300 °C for sample M3.

Figure 9 shows that the chemical shift corresponding to aluminum octahedral environments in route M1 decreased from 900 to 1200 °C, when it became identical to that of orthorhombic mullite. This decrease was due to a progressive enrichment in Si atoms in the vicinity of Al octahedra; a similar effect was observed for Al tetrahedra. The results summarized in Figure 9 indicate that the process of mullite transformation from 950 °C to well-crystallized mullite at 1200 °C was smooth and continuous for route M1. In route M2, the ^{27}Al chemical shift of Al^{VI} sites increased between 900 and 950 °C, as did the Al^{IV} chemical shift, due to segregation into alumina-rich and silica-rich regions. The Al^{VI} chemical shift increased up to 4 ppm at 1100 °C, similar to sample M3 and to θ-alumina. Above 1100 °C, the decrease reflected the intimate mixing of Al and Si atoms due to mullitization. In route M3, a continuous decrease of the chemical shift was observed, consistent with a progressive transformation from γ- to δ- and θ-type structures and mixing of Al and Si atoms. At 1300 °C, the Al^{VI} chemical shift was still somewhat different from that of orthorhombic mullite.

Drop Solution Calorimetry. Table 1 gives the heats of drop solution of transitional aluminas. Boehmite was heated to different temperatures, and the structures were verified using X-ray diffraction analysis. It was hard to get pure δ- or θ-alumina by heating boehmite: at 950 °C, only the δ phase was obtained, then at 1020 °C, a mixture of δ and θ was obtained. At higher temperature (1050 °C), the X-ray diffraction patterns show a mixture of θ- and α-aluminas, and at 1150 °C, only α alumina is observed. The enthalpy of drop solution of the combined δ- and θ-aluminas was the same as for the δ-alumina, indicating that the enthalpies of δ- and θ-aluminas must be quite similar. We employed literature values for the heats of

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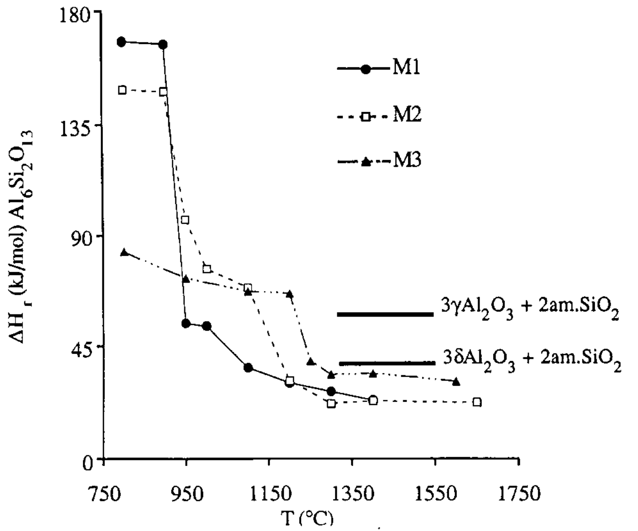

Figure 10. ΔH_r (kJ/mol of $Al_6Si_2O_{13}$) of samples M1, M2, and M3 as a function of annealing temperature. Samples are annealed for 6 h at the specified temperature. Enthalpies are heats of formation of the annealed sample from α-alumina and fused silica glass.

drop solution of amorphous silica (30 kJ/mol of SiO_2)[39] and quartz (40 kJ/mol of SiO_2)[53] in our analysis.

The heats of drop solution of samples M1, M2, and M3 heated at different temperatures from 800 to 1650 °C were measured. The standard deviation for 6–8 drops of each sample is between 2 and 3.5% for all samples. The heats of drop solution are expressed in kJ/mol and $Al_6Si_2O_{13}$; the formula describes the composition of the entire sample, which can be amorphous or mixtures of several phases (spinel, mullite, silica).

We calculated the enthalpy of formation of the samples from α alumina and amorphous silica, which is the enthalpy ΔH_r of the reaction

$$3\alpha\text{-}Al_2O_3 + 2 \text{ amorphous } SiO_2 \rightarrow \text{sample } Al_6Si_2O_{13} \quad (2)$$

$$\Delta H_r(\text{sample}) = 3\Delta H_{\text{dsoln}}(\alpha\text{-}Al_2O_3) + 2\Delta H_{\text{dsoln}}(SiO_2) - \Delta H_{\text{dsoln}}(\text{sample}) \quad (3)$$

The more positive the ΔH_r value is, the less stable the material is, relative to α alumina plus amorphous silica. Figure 10 shows ΔH_r of samples M1, M2, and M3 as a function of firing temperature.

Discussion

Exotherm at 980 °C. The exotherm ca. 980 °C in DTA was due to crystallization of mullite and/or spinel. Many results show that the existence of an exotherm at 980 °C is related to the transformation of pentacoordinated Al atoms to more stable tetrahedral and octahedral coordinations (refs 32 and 33 and this paper). In synthesis routes M1 and M2, pentacoordinated aluminum sites were present at 900 °C and an exotherm was observed at 980 °C. In route M3, pentacoordinated aluminum sites were absent, and no exothermic reaction was observed at 980 °C. Furthermore, results presented here showed that when pentacoordinated Al atoms were the dominant Al environments in the amorphous material at 900 °C (just before crystallization), mullite crystallization was preferred to crystallization of a spinel phase. Taylor[33] showed the amount of five-coordinated aluminum atoms in the *xerogels* was related to the mullite to spinel ratio after heating to 980 °C. Our results indicate that the aluminum distribution after firing at 900 °C, just before crystallization, may be more critical than the aluminum distribution in the gel. We found that the aluminum distributions in precursors M1 and M2 are very similar, but they are different at 900 °C and the dominant phases formed at 950 °C are different. Preliminary studies of alumina-rich aluminosilicates (Al/Si varying from 3 to 24)[54] support these correlations.

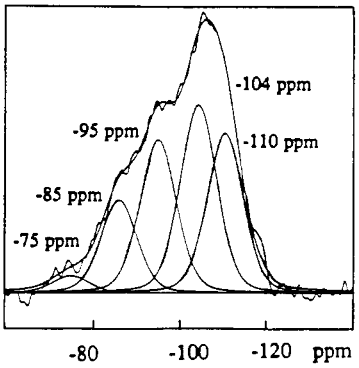

Figure 11. Simulated ^{29}Si MAS NMR spectrum of M2 fired at 1000 °C. The experimental peak was fit by contributions from $Si(OSi)_4$ at −110 ppm, $Si(OSi)_3(OAl)$ at −104 ppm, $Si(OSi)_2(OAl)_2$ at −95 ppm, $Si(OSi)(OAl)_3$ at −85 ppm, $Si(OAl)_4$ at −75 ppm.

Determination of the Spinel Phase Composition. Sample M2 annealed at 1000 °C consisted of two phases: a silica-rich phase and a spinel phase. The ^{29}Si NMR spectrum of this sample has been simulated (Figure 11): 58 at. % of the silicon atoms form the silica-rich phase (signals centered at δ = −104 and −110 ppm were due to $Si(OAl)(OSi)_3$ and $Si(OSi)_4$ sites), 25 at. % of the Si atoms belonged to the interface between the spinel crystals and the amorphous silica-rich phase ($Si(OSi)_2(OAl)_2$ sites at −95 ppm) and 18 at. % were present in the spinel phase ($Si(OAl)_3(OSi)$ and $Si(OAl)_4$ sites from signals at −85 to −75 ppm). The composition of the spinel phase was calculated from the silicon site proportions. The silica-rich phase was assumed to be pure silica (the aluminum content in the silica was considered to be negligible). Accordingly, we find the spinel composition in M2 at 1000 °C to be $Al_6Si_{0.36}O_{9.72}$, i.e., the spinel has an Al/Si ratio of 17 corresponding to about 7 wt % in SiO_2. The composition of the spinel phase has been controversial with proposed compositions varying between 0 and 50 wt % of SiO_2. Our result is in good agreement with Aksay's[34] and Okada's[8] results.

Description of the Structural Evolution. The structures of the materials were investigated locally and globally by solid-state NMR and X-ray diffraction. The ^{29}Si NMR study has led to a quantitative description of the multiphased materials.

Route M1: Direct mullitization in concert with silica segregation was observed at 950 °C for a homogeneous aluminosilicate gel. Some spinel phase was present from 950 to 1100 °C for short annealing times (6 h), but after longer annealing the spinel is converted to mullite. The spinel phase was richer in alumina than the mullite phase when the two phases coexisted.

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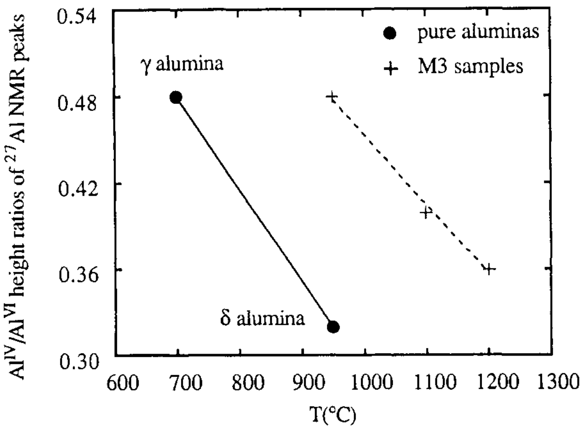

Figure 12. Al^{IV}/Al^{VI} height ratios of the ^{27}Al NMR peaks in pure alumina phases and in M3 samples.

The reaction between amorphous silica and crystals of orthorhombic mullite resulted in the continuous compositional variation of mullites. The Al/Si ratio of mullite formed around 980 °C was Al/Si = 5. The Al/Si ratio in mullites decreased with temperature as demonstrated by the decrease of the lattice parameters and unit-cell volumes, the ^{27}Al NMR chemical shifts of aluminum tetrahedral and octahedral environments and the amount of silicon atoms in the silica-rich phase. Silica was utilized for the substitution process of

$$Si^{4+} + {}^{1}/_{2}O^{2-} \leftrightarrow Al^{3+} + {}^{1}/_{2}\ \text{vacancy}$$

in order to achieve the formation of equilibrium (3:2) mullite.

Route M2: When the TEOS and AiP are hydrolyzed together, the resulting gel was less homogeneous because the aluminum alkoxide reacts more quickly. The DTA exotherm at ca. 980 °C corresponded to the transformation of an amorphous phase into spinel (Al/Si = 8)[17] and silica phases. In this route, the spinel phase did not transform into mullite after annealing for 24 h below 1100 °C. The crystalline phase transformation from a γ-type structure into δ- and θ-type structures was shown by XRD and confirmed by ^{27}Al NMR and drop solution calorimetry. Mullitization occurred at 1200 °C, but the composition of mullite crystals (Al/Si = 3.4) was still different from the bulk composition. The equilibrium state was reached around 1400 °C.

Route M3: Segregated silica- and alumina-rich regions were present all the way from the precursor to 1200 °C. Nevertheless, Si–O–Al bonds were detected at the interface of the segregated domains by ^{29}Si NMR. This slight mixing could be responsible for the delayed temperatures of crystallization of the different transitional γ- and δ-type structures compared to those of pure alumina phases.[12,14] The transformation of the γ-phase into δ- and θ-phases was observed by X-ray diffraction and also by ^{27}Al NMR. The Al^{IV}/Al^{VI} ratio decreased from about 0.48 to 0.36, and this evolution was similar to that observed in the successive transitions of pure alumina (Figure 12). The local environment changed as shown by the ^{27}Al NMR chemical shifts for both the tetrahedral and octahedral sites, which progressively shifted downfield as the annealing temperature increased from 950 to 1200 °C. Mullitization occurred at 1250 °C.

Energetics. *Enthalpy changes in the different mullitization processes*: The enthalpies of formation of the samples M1, M2, and M3 from α-alumina and fused silica glass as functions of the annealing temperature are compared in Figure 10. At 900 °C, the product from the least homogeneous gel, M3, was thermodynamically much more stable than samples M2 and M1 annealed at the same temperature. This was the result of partial crystallization of boehmite in sample M3 to γ-alumina, while M2 and M1 were amorphous. The amorphous structure M1 at 900 °C was less stable by about 20 kJ/mol than the equivalent structure M2, which is consistent with the five-coordinated Al sites being more numerous in amorphous material M1 than in M2.

An abrupt decrease in enthalpy of 112 kJ/mol for M1 between 900 and 950 °C was associated with all the structural changes occurring at this temperature: the transformation of five-coordinated aluminum sites into more stable environments, the crystallization of alumina-rich mullite and the segregation of a silica-rich phase. Between 950 and 1400 °C, ΔH_r showed a decrease of about 30 kJ/mol due to the reaction between the silica-rich phase and mullite crystals forming larger mullite crystals which were less rich in alumina. ΔH_r(M1) was almost constant above 1400 °C.

In route M2, between 900 and 950 °C, the enthalpy change of −51 kJ/mol was due to crystallization of the spinel phase and segregation of a silica-rich phase. This enthalpy change was smaller than that observed in M1 route. The enthalpy difference between M2 fired at 1000 °C and an equivalent mechanical mixture of γ-alumina and amorphous silica can be calculated (eq 4). The positive

$$3\Delta H_{\mathrm{dsoln}}(\gamma\text{-alumina}) + 2\Delta H_{\mathrm{dsoln}}(\text{am.silica}) - \Delta H_{\mathrm{dsoln}}(\text{M2–1000 °C}) = 27\ \text{kJ/mol of}\ Al_6Si_2O_{13} \quad (4)$$

enthalpy shows that a mixture of spinel plus silica-rich phase is less stable energetically than the mixture of completely segregated alumina and silica phases. The driving force for forming a spinel-type solid solution in M2, must therefore, be the configurational entropy of mixing. Mullitization from an amorphous silica-rich phase and δ-/θ-type aluminosilicate phases occurred at 1100–1250 °C with an enthalpy of −45 kJ/mol.

Enthalpies for the crystallization processes that occurred at 980 °C have been estimated from DTA. Hyatt et al.[55] estimated the enthalpy of crystallization for a sample which formed mullite, spinel, and amorphous silica at 980 °C to be −71 kJ/mol. A value of −106 kJ/mol was reported by Sen et al.[56] for a monophasic xerogel, which crystallized to mullite. These values agree with our results, −112 kJ/mol for mullite formation (route M1) and −51 kJ/mol for spinel formation (route M2) from amorphous samples annealed at 900 °C. Intermediate routes exist between M1 and M2 with intermediate values of $\Delta H_{\mathrm{crystallization}}$ at 980 °C corresponding to formation of mullite and spinel in various proportions.

In route M3, the material gradually became more energetically stable when fired from 800 to 1200 °C. This increased stability (Figure 10) paralleled the increased thermodynamic stability of the different transitional aluminas (γ, then δ and θ). M3 annealed at 1200 °C was a mixture of a δ-type phase and a silica-rich phase. This material was less stable energetically than a mixture of segregated δ-alumina plus silica, suggesting a positive

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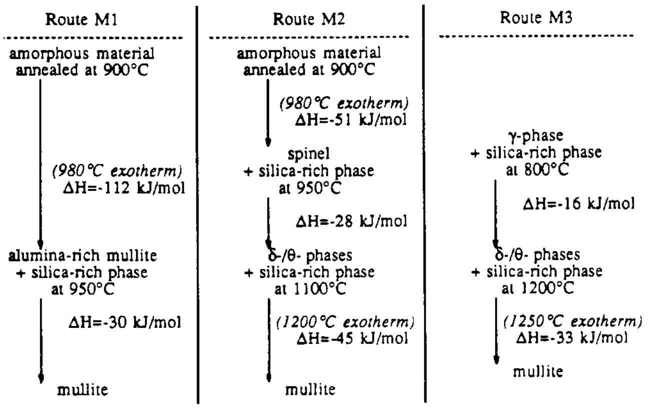

Figure 13. Schematic representations for the phase transformations and the energetics in the evolutions of mullite formation.

enthalpy of mixing of alumina and silica. The enthalpy change of −33 kJ/mol between 1200 and 1300 °C resulted from the reaction between the amorphous silica-rich phase and the crystalline alumina-rich phase to form mullite. This mullitization enthalpy was comparable to that in route M2. The DTA exotherms between 1200 and 1250 °C in routes M2 and M3 probably resulted from similar structural transformations. It has been reported that mullite forms from δ-alumina plus silica[12,13] or from θ-alumina plus silica.[31] The exothermic reaction around 1250 °C for M3 led to the formation of a mullite phase which was energetically less stable by 10 kJ/mol than mullites M1 and M2 formed at 1250 °C. This accounts for the difference in the enthalpy of mullitization between M2 and M3 (see Figure 13), and may be related to the different Al/Si ratios characterizing mullite crystals in M1 and M2 (Al/Si = 3.2) and in M3 (Al/Si = 2.9).

Figure 13 summarizes the phase transformations and the energetics in the evolutions of mullite formation. The temperatures for the transitions as detected by DTA are reported: no exotherm was detected in DTA for the substitution process from alumina-rich mullite to equilibrium (3:2) mullite because of a slow reaction occurring over a large range of temperature. Also, no exotherm is detectable by standard DTA for the transitions from γ- to δ-/θ-type structures in routes M2 and M3.

Stable mullite solid solution: The drop solution calorimetry experiments permit direct comparison of the relative stability of the materials formed by the different processes. The enthalpies of formation of the mullites from a mixture of α-alumina and fused silica (or quartz) were all endothermic. The enthalpies, ΔH_r, at 1400 °C (Figure 10) were 29 kJ/mol of $Al_6Si_2O_{13}$ for M1 and M2 (50 kJ/mol from quartz), and 40 kJ/mol of $Al_6Si_2O_{13}$ for M3 (61 kJ/mol from quartz). The endothermic enthalpies suggest that mullites are entropically stabilized by the configurational entropy associated with the disorder of Al/Si cations and vacancy/oxygen sites, as suggested by previous observations.[57,58]

The XRD data indicated that the mullite Al/Si ratio varied with the preparation route. Pask et al.[59] also observed that the nature of the starting materials determined the phase composition of the final mullite microstructures. The effect of Al/Si ratio in the mullite phase on the thermodynamic stability of the mullite wax examined by determining the relative enthalpy of mullites as a function of the Al/Si ratio. The Al/Si of mullite crystals was determined by X-ray diffraction and Cameron's relation. Only ΔH_r of mullites M1, M2, and M3 heated at high temperatures ($T > 1300$ °C) were used for this correlation and all the samples had a bulk composition corresponding to Al/Si = 3. The results shown in Figure 14 show that samples heated at high temperature were made of mullite crystals having Al/Si ratios ranging from about 2.9 to about 3.5, or equivalently 71.1 to 74.8 wt % Al_2O_3, in good agreement with the equilibrium mullite solid-solution limits found by Aramaki and Roy[23] and Aksay and Pask.[27] Figure 14 shows that mullite crystals having Al/Si of about 3.2 had the lowest enthalpy, suggesting that Al/Si = 3.2, or equivalently 73 wt % Al_2O_3, corresponded to the most stable composition of mullite.

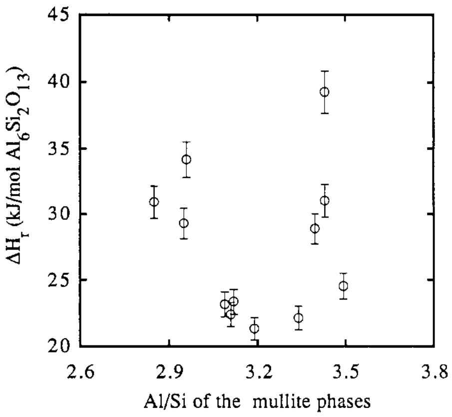

Figure 14. ΔH_r (kJ/mol of $Al_6Si_2O_{13}$) of samples M1, M2, and M3 (heated at higher temperature than 1300 °C) as a function of the mullite Al/Si ratio. Heat of reaction to form mullite from α-alumina and fused silica. The composition of the mullite phase was determined from the lattice parameter using the correlation given in eq 1.

Metastable mullite solid solution: In route M1, alumina-rich mullite forms at low temperature and gradually transforms into equilibium mullite with increasing temperature. The samples M1 annealed at 950, 1000, and 1100 °C for 24 h and the samples annealed for 6 h above 1150 °C are two-phase materials consisting of a silica phase and a mullite phase, with the combined stoichiometry fixed as $Al_6Si_2O_{13}$. The Al/Si ratio in the mullite phase was determined from XRD by the correlation of lattice parameter with stoichiometry. Assuming all the aluminum is in the mullite phase the amount of the silica phase present was found by mass balance using eq 5. The value

$$Al_6Si_2O_{13} = (6/x)[Al_xSiO_{2+1.5x} + (x/3 - 1)SiO_2] \quad (5)$$

of x decreases from about 5 at 950 °C to about 3 at 1400 °C. Assuming that the amorphous silica phase is energetically equivalent to fused silica, enthalpies of formation of $Al_xSiO_{2+1.5x}$ compounds were determined and are shown in Figure 15. Cameron[36] proposed a continuous solid solution for mullite $Al^{VI}_2[Al^{IV}_{2+2z}Si^{IV}_{2-2z}]O_{10-z}$ of $z = 0.17$–0.59 on the basis of a smooth variation of the lattice parameters, where z is the number of oxygen atoms missing per unit cell. This range of composition lies from 69 to 84 wt % Al_2O_3, corresponding to Al/Si varying from 2.6 to 6.3. The maximum alumina content of 84 wt % in

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(59) Pask, J. A.; Zhang, X. W.; Tomsia, A. P.; Yoldas, B. E. *J. Am. Ceram. Soc.* **1987**, *70*, 704.

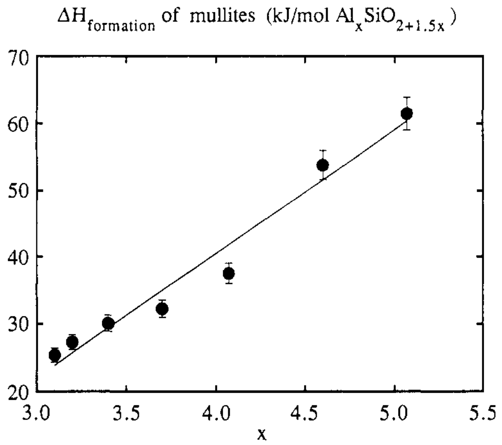

Figure 15. Enthalpies of formation of mullites $Al_xSiO_{2+1.5x}$ as a function of x. The heats of formation of the mullites from α-alumina and quartz. The composition of the mullite phase was determined from the lattice parameter using the correlation given in eq 1.

mullite was reported by several workers.[24,25,27,60] The enthalpy of formation of $Al_xSiO_{2+1.5x}$ mullites, shown in Figure 15, is linearly correlated with composition:

$$\Delta H_{formation}(Al_xSiO_{2+1.5x}) = 18.4x - 33.1 \text{ kJ/mol} \quad (6)$$

The enthalpy ΔH_{Al-Si} of the substitution reaction 7 was calculated from the enthalpy of the exchange reaction 8.

$$Si^{4+} + {}^1/_2O^{2-} \rightarrow Al^{3+} + {}^1/_2 \text{ vacancy} \quad (7)$$

$$Al_ySi_xO_{2x+1.5y} \rightarrow Al_{y+1}Si_{x-1}O_{2x+1.5y-0.5} \quad (8)$$

$$\Delta H_{Al-Si} = \Delta H_f(Al_{y+1}Si_{x-1}O_{2x-1}O_{2x+1.5y-0.5}) - \Delta H_f(Al_ySi_xO_{2x+1.5y}) \quad (9)$$

ΔH_{Al-Si} equals 52 kJ/mol. Holm and Kleppa[58] determined the heats of solution of mullite $Al_6Si_2O_{13}$ and sillimanite, which is the high-pressure Al_2SiO_5 polymorph. From the two values of heats of solution corresponding to Al/Si = 3 and Al/Si = 2, they determined a heat of reaction for the substitution reaction 7 of 59 kJ/mol and noted that this value was approximately the difference in heat of formation between 0.5 mol of Al_2O_3 and 1 mol of SiO_2, which is 57 mJ/mol at 1200 °C. The value of 52 kJ/mol estimated in the present study suggests that the difference in heats of formation between mullites of different compositions may also be attributed to the difference between Si–O and Al–O bond energies.

Conclusions

A systematic study of stoichiometric mullite precursors (Al/Si = 3) prepared in three different ways investigated the compositional, structural, and thermochemical changes from the precursors to completely crystallized mullites. The significant results are as follows.

Mullitization, spinel formation, and silica segregation can occur in concert leading to the exothermic transformation around 980 °C of an amorphous phase into a partly crystalline multiphased material. The 980 °C DTA exotherm has its origin in the transformation of metastable pentacoordinated aluminum sites present in the amorphous phase.

(ii) Mullitization is preferred to spinel crystallization when the pentacoordinated Al sites are the predominant Al environments in the amorphous phase at 900 °C.

(iii) The alumina-rich spinel was determined to contain about 7 wt % SiO_2 based on ^{29}Si NMR.

(iv) ^{29}Si and ^{27}Al NMR revealed the presence of Si–O–Al bonds, which created a positive enthalpy of mixing as indicated by high-temperature drop solution calorimetry.

(v) The more homogeneous the Al–Si mixing at 900 °C, as indicated by NMR, the larger the crystallization enthalpy and the lower the mullitization temperature. The mullitization enthalpy varied from −112 kJ/mol in the most homogeneous sample (around 980 °C) to −33 kJ/mol in the least homogeneous sample (around 1250 °C).

(iv) When mullitization occurred at low temperature, a continuous process of transformation of mullite crystals occurred with increasing temperature from 950 to 1400 °C; the reaction between silica and mullite forms more stable mullite crystals with lower Al/Si ratios.

(vii) The enthalpy of the substitution reaction, $Al^{3+} + {}^1/_2$ vacancy $\rightarrow Si^{4+} + {}^1/_2O^{2-}$, responsible for the compositional change in mullites was −52 kJ/mol.

(viii) The mullite composition with the lowest enthalpy of formation had an Al/Si ratio of 3.2.

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