Journal of the European Ceramic Society **11** (1993) 87–94

Mullite Precursor Phases

H. Schneider, B. Saruhan, D. Voll
German Aerospace Establishment, Institute for Materials Research, 5000 Köln 90, Germany

L. Merwin* & A. Sebald
Bavarian Institute for Geosciences, University of Bayreuth, 8580 Bayreuth, Germany

(Received 20 December 1991; revised version received 9 March 1992; accepted 9 April 1992)

Abstract

Admixtures of tetraethoxysilane (TEOS) and aluminium sec.*-butylate (AlOBu) with stoichiometric* $3Al_2O_3 . 2SiO_2$ *mullite composition were used for the syntheses. Depending on the amount of* H_2O, *the velocity of the hydrolysis process and the pH of the solvent, three different types of temperature-induced mullite formation processes are observed.*

Type I mullite precursors: produced by slow hydrolysis with very little H_2O. *From* $\approx 350°C$ *and up to* $\approx 900°C$ *these precursors are non-crystalline and show a homogeneous mixture on an atomic level. Above this temperature limit the precursors transform to* Al_2O_3*-rich mullite and non-crystalline* SiO_2.

Type II mullite precursors: produced by rapid hydrolysis with excess H_2O *in a very basic environment* ($pH > 10$). *Above* $\approx 350°C$ *these precursors are more phasic, consisting of relatively large crystalline* γ-Al_2O_3, *and of non-crystalline* SiO_2*-rich areas. Mullite formation is observed at* $\gtrsim 1200°C$.

Type III mullite precursors: produced by rapid hydrolysis with excess H_2O *in a moderately basic environment* ($pH \leq 10$). *From* $\approx 350°C$ *and up to* $\approx 900°C$ *these precursors are non-crystalline. Above this temperature limit the precursors gradually transform to* γ-Al_2O_3 *and non-crystalline* SiO_2*-rich areas. Mullite formation is observed at* $\gtrsim 1200°C$.

Mischungen aus Tetraethoxysilan (TEOS) und Aluminium sek.*-butoxid (AlOBu) mit stöchiometrischer Mullitzusammensetzung* ($3Al_2O_3 . 2SiO_2$) *wurden für die Synthesen verwendet. Abhängig von der vorhandenen Menge an* H_2O, *der Hydrolysegeschwindigkeit und vom pH-Wert des Lösungsmittels beobachtet man drei unterschiedliche, temperaturabhängige Mullitbildungsprozesse.*

Typ I-Mullit-Precursoren, die über langsame Hydrolyse in Gegenwart von sehr wenig H_2O *entstehen. Von* $\approx 350°C$ *bis* $\approx 900°C$ *zeigen diese nichtkristallinen Precursoren eine im atomaren Maßstab homogene Mischung. Oberhalb dieser Temperaturen zerfallen die Precursoren zu* Al_2O_3*-reichem Mullit und nichtkristallinem* SiO_2.

Typ II-Mullit-Precursoren, die über schnelle Hydrolyse in Gegenwart von überschüssigem H_2O *in sehr basischer Umgebung* ($pH > 10$) *entstehen. Oberhalb* $\approx 350°C$ *sind diese Precursoren mehrphasig und bestehen aus relativ großen* γ-Al_2O_3*-Kristalliten und aus nichtkristallinen* SiO_2*-reichen Bereichen. Mullitbildung wird oberhalb* $\approx 1200°C$ *beobachtet.*

Typ III-Mullit-Precursoren, die über schnelle Hydrolyse in Gegenwart von überschüssigem H_2O *in mäßig basischer Umgebung* ($pH \leq 10$) *entstehen. Von* $\approx 350°C$ *bis* $\approx 900°C$ *sind diese Precursoren nichtkristallinen. Oberhalb dieser Temperaturen zerfallen die Precursoren graduell in* γ-Al_2O_3 *und nichtkristalline* SiO_2*-reiche Bereiche. Mullitbildung wird oberhalb* $\gtrsim 1200°C$ *beobachtet.*

Des mélanges de tetraethoxysilane (TEOS) et de butylate d'aluminium secondaire (AlOBu), de stoechiométrie correspondant à la mullite ($3Al_2O_3 . 2SiO_2$) *ont été utilisés pour la synthèse. Selon la quantité d'eau utilisée, la vitesse d'hydrolyse et le pH du solvent, on observe, avec la température, trois processus différents de formation de la mullite.*

Les précurseurs de mullite du type I sont obtenus par hydrolyse lente en présence d'une quantité réduite d'eau. De environ $350°C$ *à* $900°C$, *ces précurseurs sont amorphes et parfaitement homogènes au niveau répartition atomique. Au delà de cette dernière température, les précurseurs se transforment en mullite riche en* Al_2O_3 *et* SiO_2 *amorphe.*

Les precurseurs mullitiques type II sont produits par une hydrolyse rapide avec un excès d'H_2O *et dans un environnement très basique* ($pH > 10$). *Au-dessus*

---

*Present address: Naval Weapons Center, Code 3851 Michelson Lab, China Lake, California 93555, USA.

Journal of the European Ceramic Society 0955-2219/93/$6.00

de 350°C, ces précurseurs contiennent plusieurs phases, ils sont composés en forte proportion de γ-Al_2O_3 à structure cristalline et de régions riches en SiO_2 amorphe. La formation mullitique est observée à >1200°C.

Les précurseurs mullitiques de type III sont produits par une hydrolyse rapide avec un excès d'H_2O et dans un environnement basique modéré ($pH \leq 10$). De environ ≈350°C à ≈900°C, ces précurseurs sont amorphes. Au-dessus de cette température limite, les précurseurs se transforment petit à petit en γ-Al_2O_3 et SiO_2 amorphe. La transformation mullitique est observée à ≳1200°C.

1 Introduction

Mullite ($3Al_2O_3.2SiO_2$) has been the object of intensive research in recent years, due to its excellent properties, such as high creep resistance, low thermal expansion and good chemical stability.[1] Researchers dealing with mullite synthesis have reported various methods and sources. Mainly four types of starting materials for mullite synthesis are recognized:

—Oxides or hydroxides.
—Sols.
—Metal salts.
—Metal alkoxides.

Different combinations of these starting materials lead to mullite; however, the reaction process during mullite formation differs. Solid mixtures of oxides or hydroxides require higher temperatures (>1450°C) for a quantitative formation of mullite.[2] By the application of sols as starting material, the mullitization temperature can be reduced to 1200–1300°C.[3] Combinations of Si-sols and Al-salt solutions (e.g. $Al_2(SO_4)_3$, $Al(NO_3)_3$, etc.) are reported to form γ-Al_2O_3 spinels at temperatures ≥1000°C.[4,5] Combinations of Si- and Al-salt solutions follow a similar trend, although, depending on the process temperature during synthesis, boehmite or bayerite may form.[6] Some exceptions which yield mullite with these combinations at around 950°C are known.[7,8] In order to achieve a mullitization temperature below 1000°C, it appears to be necessary to choose a combination of a salt and an alkoxide, or metal alkoxides for both compounds.[3,9,10]

The frequent formation of a cubic γ-Al_2O_3 phase as an intermediate phase during mullite formation has engaged many studies. There has been much controversy about the composition and the identity of this phase. Komarneni & Roy[11] and Brown *et al.*[12] concluded after various MAS NMR and lattice parameter measurements that the cubic γ-Al_2O_3 phase is virtually pure Al_2O_3, while Chakravorty & Ghosh[5] reported that it is an Al–Si spinel. Low & McPherson,[13] in their comprehensive study, indicated that an Al–Si spinel with a composition similar to that of $2Al_2O_3.SiO_2$ mullite forms primarily and may gradually reorder to $3Al_2O_3.2SiO_2$ mullite. Schneider *et al.*[14] showed later on that the γ-Al_2O_3-type phase may contain some Si; however, the amount of Si is much lower than that postulated by Chakravorty & Ghosh.[5]

Similarly to the above controversy, the composition of mullite formed at lower temperatures between 1000 and 1400°C has been discussed often. It is generally believed that this phase is an Al_2O_3-rich mullite. At higher temperatures (>1400°C) a gradual transformation to stable stoichiometric mullite is observed.[9,13–17] It is not the aim of this paper to become involved in these discussions, rather it is to deal with the determination of synthesis routes obtained by using the same starting materials, to characterize the structure of the resulting mullite precursors, and to describe the reaction processes occurring during thermal treatments.

2 Experimental Methods

2.1 Differential thermal analysis (DTA)

Differential thermal analysis and thermal gravity measurements were performed with a computer-controlled Netzsch STA 409 apparatus (sensitivity: 50 mV). About 80 mg of the samples and of the reference material (fired kaolinite), respectively, were heated in Pt crucibles, with a constant heating rate of 10 K/min. All DTA and TG runs were carried out in air.

2.2 X-ray diffractometry (XRD)

X-ray powder diffraction studies were carried out at room temperature with a computer-controlled Siemens D5000 powder diffractometer using Ni-filtered CuK_α radiation. Diffraction patterns were recorded in the 10° to 80° 2θ range, in the step scan mode (3 s/0·02°, 2θ).

2.3 ^{29}Si MAS nuclear magnetic resonance (NMR)

All ^{29}Si MAS spectra have been obtained at an operating frequency of 59·6 MHz, using a Bruker MSL 300 NMR spectrometer equipped with double-bearing probes. All samples were packed in 7 mm o.d. ZrO_2 rotors; spinning rates were 3·2–4·1 kHz. Relaxation delays of 30–60 s and pulse width of 2–3 μs (= 36–54° pulses) were adequate experimental conditions to exclude alteration due to ^{29}Si relaxation. Between 300 and 2500 transients had to be accumulated, depending on the line width and the relaxation characteristics of the various samples.

Exponential line broadening of 25 Hz was used in all cases prior to Fourier transformation (with half-height line width of >400 Hz in all cases, a line broadening factor of 25 Hz will not cause any undue distortions of line shape resolution). Since some of these precursor phases are not exactly easy to pack and spin, great care was taken to avoid a spin-down of the probe.

3 Sample Preparation

All precursors are prepared by using tetraethoxysilane (TEOS) and aluminium *sec*.-butylate (AlOBu) as starting materials. Si- and Al-alkoxides were admixed in proportions corresponding to stoichiometric mullite ($3Al_2O_3 . 2SiO_2$) in each case. According to the synthesis conditions and the precursor properties, samples are identified in three groups, designated as type I, type II and type III.

3.1 Type I precursor (sample NH)

The metal alkoxides were diluted with isopropanol and mixed with each other. Hydrolysis of the mixed solutions was initiated only by air contact over several days, in a glove box. The hydrolysis duration was approximately 14 days. Condensation and polymerization of this mixture lead to the formation of a homogeneous network of atomic linkage of –Si–O–Al–O–Si–, where Al- and Si-atoms are statistically distributed.

According to Yoldas,[10] the following reaction can be considered as a typical example for type I precursors:

$$\underset{(\mathrm{AlOBu})}{\mathrm{Al(OR')_3}} + \underset{(\mathrm{TMOS, TEOS})}{\mathrm{Si(OR)_4}} + \mathrm{SLV} + \mathrm{H_2O} \xrightarrow{\text{(humified air)}} \mathrm{(OR')_2Al{-}O{-}Si(OR)_3} + \mathrm{R'OH} + \mathrm{ROH}$$

where SLV = solvent (alcohol); TMOS = tetramethoxysilane; R,R′ = organic groups.

The type I sample is designated as NH in the text for simplicity and corresponds to no prehydrolysis.

3.2 Type II precursor (sample HB13)

TEOS was mixed with an appropriate portion of isopropanol and water under strongly basic conditions (pH = 13), in order to prehydrolyse TEOS fully. Prehydrolysis was carried out, mainly because of the lower hydrolysis rate of TEOS compared to that of AlOBu. After a short reaction time, this TEOS solution was mixed with AlOBu solution, which was already diluted with isopropanol. The mixed solution gellified immediately. The following reaction shows that full prehydrolysis of TEOS yields monomeric silica ($Si(OH)_4$):

$$\mathrm{Si(OR)_4} + \text{excess } \mathrm{H_2O} \xrightarrow{\mathrm{pH} \geq 10} \mathrm{Si(OH)_4} + \mathrm{H_2O}$$

The TEOS solution after hydrolysis under these conditions contains excess water. On mixing this solution with AlOBu solution, this excess water immediately hydrolyses AlOBu and forms large colloids with a composition similar to pseudo-boehmite (≥100 to ≤1000 Å, as estimated by XRD line broadenings).

Type II precursors can be produced by different synthesis techniques. The Al_2O_3 source can be introduced either in the form of a sol[10] or can originate from salts through a chemical process.[4,6] The third technique involves full hydrolysis of Si-alkoxide, as already described, or rapid hydrolysis of sol mixtures, and in both cases the process is controlled by the pH value.

The common character of type II precursors is that large colloidal particles of Al-oxyhydrate are produced which coexist with amorphous monomeric Si-rich areas:

$$\mathrm{Si(OH)_4} + \mathrm{Al(OR')_3} + \mathrm{SLV} + \text{excess } \mathrm{H_2O} \xrightarrow{\mathrm{pH} \geq 10} \mathrm{AlO(OH)} + \mathrm{Si(OH)_4}$$

Monomeric silica has a strong tendency of being absorbed onto the surfaces of the AlO(OH), the absorption rate being dependent on the pH value and surface area.[18] This leads to the formation of alumina colloids surrounded by Si-rich areas and to the diffusion of Si into the colloids as the temperature increases, during burn-out of the organic groups.

The type II sample is designated as HB13, which stands for prehydrolysed under basic conditions with pH = 13.

3.3 Type III precursor (sample HB10)

For this sample a similar synthesis procedure as for sample HB13 was applied. However, synthesis was carried out under a less basic condition (pH = 10) and the sample is designated as HB10.

According to Iler,[18] above pH = 6 or 7 up to 10·5, where SiO_2 begins to dissolve as silicate, the hydrous silica particles are negatively charged and repel each other. Hence, the reaction prevents the polymerization of hydrolysed SiO_2 and inhibits the evolution of excess water. Therefore, further mixing with the AlOBu solution does not produce any hydrolysis of the latter, which would otherwise give rise to the formation of crystalline oxyhydrate phases.

4 Results

4.1 Differential thermal analysis (DTA)

Only DTA observations of samples preheated at 350°C are described, since DTA patterns between room temperature and 350°C are complex, and are not yet fully understood. DTA-related reaction processes within this range of temperatures will be discussed in a separate study.

The DTA curves are characterized by the occurrence of exothermic peaks near 980 and/or 1250°C. Type I mullite NH precursor shows a rather sharp and strong peak at about 980°C but no peaks near 1250°C. Type II mullite HB13 precursor exhibits no DTA signals up to 1400°C. Type III mullite HB10 precursor exhibits a sharp exotherm at 980°C, but of lower intensity than type I mullite precursor. At 1250°C an additional broad peak of low intensity can be observed (Fig. 1).

4.2 X-ray diffractometry (XRD)

XRD data of the precursors in the as-received form, and calcined between 350, 900, 1000 and 1650°C, are summarized in Fig. 2(a) to (c).

Type I mullite NH precursor is non-crystalline up to 1000°C, providing rapid heating and by allowing no soaking time. Above ≈1000°C mullite appears either as the only crystalline phase or together with a minor amount of poorly crystallized γ-Al_2O_3 spinel (Fig. 2(a)). (Although there is some NMR evidence that γ-Al_2O_3 contains some Si, the authors believe that a rather small fraction of the Si present is incorporated and therefore it does not have the composition suggested by Chakravorty & Ghosh.[5] In the text hereafter the term γ-Al_2O_3 will be used.) Annealing experiments with long duration (15 h), carried out at 900, 930 and 960°C, indicate that mullitization is initiated above 900°C (Fig. 3).

Type II mullite HB13 precursor in the as-received form contains pseudo-boehmite. After heat treatment the material dehydrates, and is converted to γ-Al_2O_3. A gradual and temperature-dependent increase in intensity and sharpening of X-ray reflections are observed. The X-ray diffraction data of the type II precursor shows the occurrence of γ-Al_2O_3 up to 1250°C. Above this temperature limit mullite forms, together with a minor amount of corundum (Fig. 2(b)).

Type III mullite HB10 precursor is also non-crystalline up to 1000°C, after rapid heating and by allowing no soaking time. Above 1000°C the only crystalline phase is γ-Al_2O_3. Heat treatments with

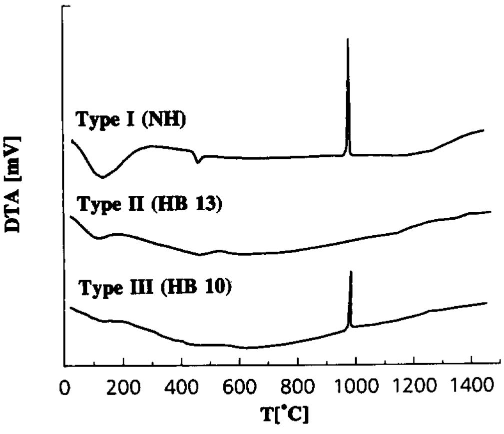


Fig. 1. Differential thermal analysis (DTA) curves of mullite precursor types I, II and III. All samples were preheated to 350°C (15 h) prior to DTA.

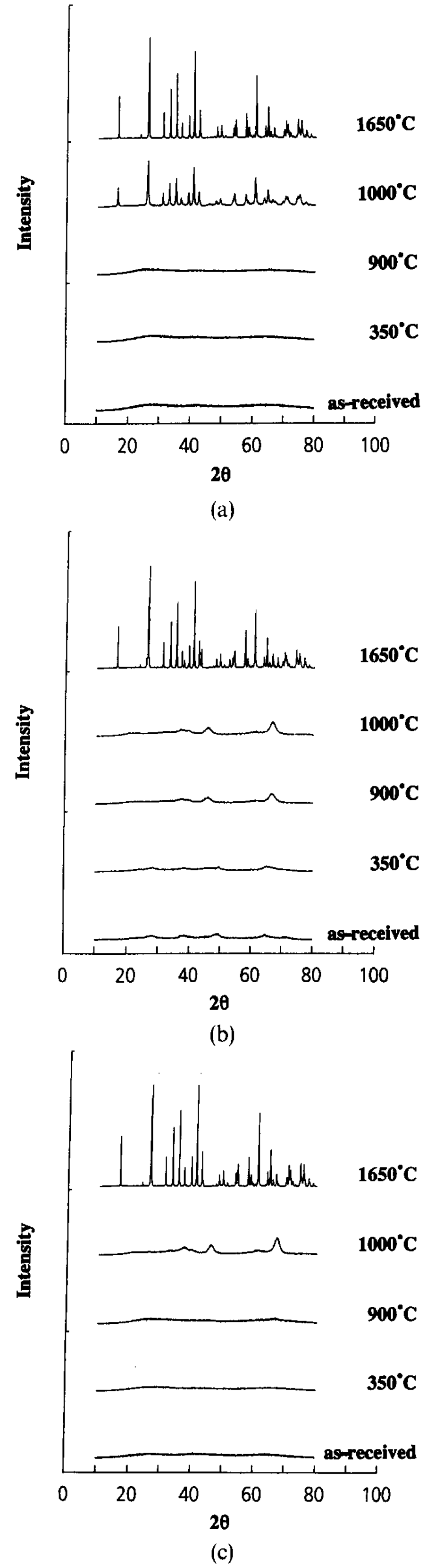


Fig. 2. X-ray diffraction (XRD) of mullite precursors, as-received and heat treated at 350, 900, 1000 and 1650°C (15 h in each case): (a) type I (NH); (b) type II (HB13); (c) type III (HB10).

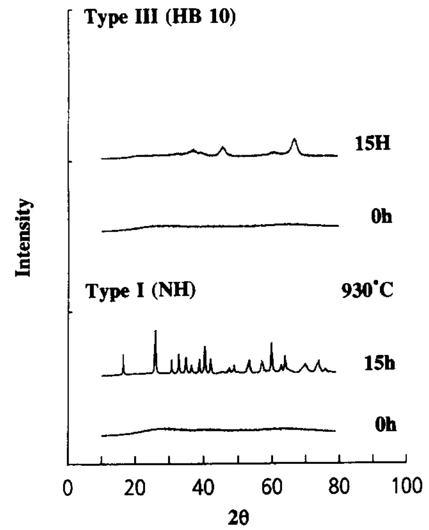


Fig. 3. X-ray diffraction (XRD) of mullite precursors type I and type III after heat treatment at 930°C with no holding time and for 15 h.

long holding times carried out in the same way as for type I precursors show partial crystallization of γ-Al_2O_3 above 900°C (Fig. 3). At temperatures above ≈1250°C mullite is formed (Fig. 2(c)).

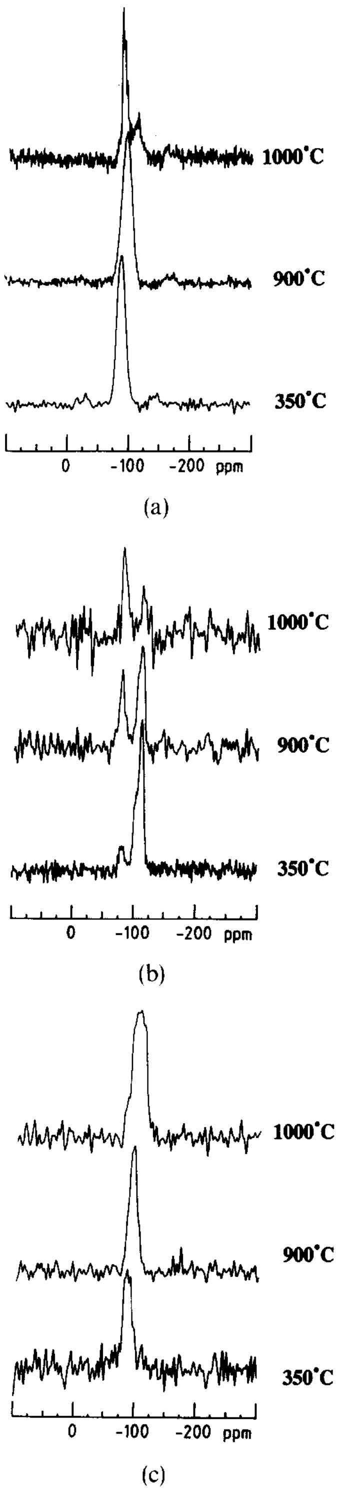
4.3 ^{29}Si MAS nuclear magnetic resonance (NMR)

The ^{29}Si MAS NMR spectra of mullite type I, II and III precursors display resonances between about −80 and −110 ppm. Quite a variation in signal intensities, line widths and fine structures is observed (Fig. 4(a) to (c)), although all ^{29}Si NMR data can be ascribed to tetrahedrally coordinated Si.

Type I mullite NH precursor heat treated at 350°C is characterized by an intense and fairly sharp and symmetric ^{29}Si resonance in the −85 ppm chemical shift region. At 900°C the ^{29}Si NMR peak shifts towards more negative values (−95 ppm) (Fig. 4(a)). At 1000°C the previously uniform ^{29}Si NMR peak alters its shape and shows two new maxima near −90 and −110 ppm. The former has the typical position and shape of a ^{29}Si NMR signal for mullite; the latter is correlated with nearly pure non-crystalline SiO_2.

Type II mullite HB13 precursor heat treated at 350°C displays ^{29}Si NMR resonances composed of two components with maxima at −80 and −110 ppm. The intensity of the −80 ppm peak is low in the sample heat treated at 350°C, while that of the −110 ppm peak is rather high. As the heat treatment temperature increases, the intensity of the −80 ppm peak also strongly increases, whereas that of the −110 ppm peak decreases (Fig. 4(b)).

Type III mullite HB10 precursor heat treated at 350°C exhibits a slightly split ^{29}Si NMR signal with a peak maximum near −85 ppm and a submaximum near −91 ppm. At 900°C the peak maximum shifts to ≈−95 ppm and simultaneously the signal becomes sharper. At 1000°C broadening and splitting of the NMR peak is observed; the peak maxima appear at ≈−80, −100 and −110 ppm (Fig. 4(c)).



(a)

(b)

(c)

Fig. 4. ^{29}Si MAS NMR spectra of mullite precursors heat treated at 350, 900 and 1000°C (15 h in each case): (a) type I (NH); (b) type II (HB13); (c) type III (HB10).

5 Discussion

The synthesis of pure type I, II and III mullite precursors, especially that of type I, is rather difficult, because the reactions which occur during synthesis are sensitive to small changes in the preparation conditions. Therefore, mostly pre-mullites are produced, which consist of a combination of two different types of precursors, rather than that of the intended end members. Generally, in literature they are named as 'diphasic' gels.[3] The samples NH, HB10 and HB13 described in this paper, however, should be regarded as the pure representatives of these precursor groups, because each consists of only one type.

5.1 Type I precursor

Type I mullite NH precursor yields DTA curves with sharp and intense exotherms at about 980°C (Fig. 1). Rapidly heated and quenched samples are non-crystalline below 1000°C and consist of alumina-rich mullite and an excess of SiO_2-rich amorphous phase (Fig. 2(b)). Long heat treatments lead to mullitization at about 930°C (Fig. 3).

^{29}Si NMR signals of the type I precursor are relatively sharp and display high intensity. NMR peaks of the sample heat treated at 350°C centre at ≈ -85 ppm, while for the precursor heat treated at 900°C they appear at ≈ -95 ppm (Fig. 3(a)). According to the studies of Mägi *et al.*[19] and Engelhardt & Michel,[20] the position of the ^{29}Si NMR signals is controlled either by the number of the nearest Al-atoms around Si or by the number of -Si–O–(Si,Al) bridges occurring in the structure. Making use of these considerations, the -85 ppm NMR signal of the type I sample, heat treated at 350°C, is assigned to the presence of Si with 4Al as nearest cations. The temperature-induced shifting of the ^{29}Si NMR signal of the sample heat treated at 900°C towards more negative values, however, is explained with the increase in the number of -Si–O–(Si,Al) bridges, corresponding to an increasing degree of condensation of the -Si–O–(Si,Al) network. The alternative model given suggests an increasing number of Si in the second coordination sphere around Si as the temperature increases. This would mean a phase segregation into SiO_2- and Al_2O_3-rich areas. A phase segregation in the precursor, as a result, should give rise to the formation of γ-Al_2O_3 plus SiO_2 phases instead of mullite. Since no phase segregation is observed up to 900°C, this former model can be no probable explanation for the present case.

Mullite formation from the initially amorphous type I precursor at temperatures as low as 930°C after long heat treatment, and the NMR spectra of the sample heat treated at 900°C, prove that Si is homogeneously mixed with Al and O on an atomic level. This intimate homogenization enables mullitization at that low temperature, because mullite nucleation and crystal growth require only short-distance migration of diffusion species. Some studies assume that mullite crystallization occurs only above $\approx$1000°C, independent of the duration of the heat treatment, and according to the authors this is due to the low value of proton diffusion in mullite precursors.[21,22] In another study[23] with similar types of mullite precursors, however, it is pointed out that the nucleation of mullite commences at 940°C, upon densification of the glass. The present results agree with the latter study (see Fig. 3).

5.2 Type II precursor

Type II mullite HB13 precursor yields no DTA signals (Fig. 1), indicating the lack of temperature-induced reactions. The XRD reflections of the samples heat treated at 350, 900 and 1000°C (Fig. 2(b)) indicate a phase segregation into γ-Al_2O_3-type phase and non-crystalline SiO_2-rich areas. According to X-ray line broadenings the γ-Al_2O_3 domains are relatively large in size (≥ 100 to ≤ 1000 Å) and display a certain long-range disorder. Gradual temperature-dependent intensity increase and sharpening of γ-Al_2O_3 X-ray reflections may be interpreted as due to increasing ordering and growth of γ-Al_2O_3 crystallites.

Type II mullite precursor produces ^{29}Si spectra with two main peaks centred near -80 and -110 ppm independently from the treatment temperature (Fig. 4(b)). The -110 ppm peak is due to the occurrence of a virtually pure non-crystalline SiO_2 compound. The -80 ppm peak can be ascribed to Si having four nearest Al neighbours either in an additional, although Al_2O_3-rich non-crystalline phase, or in γ-Al_2O_3,[24] or in both.[14] The intensities of NMR signals indicate that at 350°C most of the Si is bound in the non-crystalline SiO_2 phase, while a minor amount is incorporated into the Al_2O_3-rich compound. As temperature increases, the amount of the coexisting SiO_2 apparently decreases, while the amount of Si present in the Al_2O_3-rich compound does increase.

The segregation of Al_2O_3- and SiO_2-rich clusters in the type II mullite precursor causes mullitization to take place at relatively high temperatures (1150–1250°C). The lack of DTA signals implies that this mullitization is a gradual process. The probable reason is that the nucleation and crystal growth require long-distance migration of diffusion species.

5.3 Type III precursor

Type III mullite HB10 precursor yields a DTA curve with a sharp and intense exotherm at 980°C and an exothermic peak of lower intensity at about 1250°C (Fig. 1). Rapidly heated and quenched samples are X-ray amorphous below 980°C but consist of γ-Al_2O_3 plus some excess non-crystalline SiO_2-rich phase above this temperature limit. Long heat treatments yield γ-Al_2O_3 crystallization at 930°C (Figs

2(c) and 3). Mullitization of the phase admixture starts at temperatures ≥1200°C. The high mullitization temperature can be explained by the long diffusion distances necessary for crystal growth in a similar way as for the type II precursors.

Type III precursor heat treated at 350°C produces slightly split ^{29}Si MAS NMR resonances, with a peak maximum near −85 ppm, indicating a small degree of chemical heterogeneity in this material (Fig. 4(c)). After heat treatment at 900°C, the ^{29}Si NMR signal becomes sharper and the peak maximum shifts to ≈−95 ppm. This probably means that the Si distribution in the precursor becomes more homogeneous, possibly due to burn-out of the organic species and evaporation of residual water, and that the degree of condensation improves in a similar way as discussed in the type I mullite precursor.

At 1000°C a broad and non-uniform NMR signal with submaxima near −80, −100 and −110 ppm appears. This complex NMR pattern can be attributed to the beginning of a phase segregation in the previously homogeneous precursor, which produces a phase mixture of γ-Al_2O_3, a virtually pure SiO_2 and some residual precursor phase.

It is interesting to point out that, despite their very similar ^{29}Si NMR spectra and their associated similar Si short-range orders at 900°C, type I and type III mullite precursors behave differently after heat treatments above 900°C. The formation of γ-Al_2O_3 plus amorphous SiO_2 above 900°C in type III precursors suggests that phase segregation into Al_2O_3- and SiO_2-rich areas requires lower activation energy than mullite formation does. ^{27}Al NMR data of mullite precursors similar to type I and type III presented by Sanz *et al.*[25] may help to understand discrepancies. (Samples described by Sanz *et al.*[25] which are similar to type I and type III are designated as samples SP and PB_2, respectively.)

Observation of the ^{27}Al NMR spectra of a type I similar sample heat treated at 900°C shows high amounts of pentahedral Al-sites or strongly distorted tetrahedral Al-sites with excess O-neighbours.[14] On the other hand, Sanz *et al.*[25] observed a high amount of octahedral Al in the type III precursors heat treated at 900°C. The similarity of the ^{27}Al NMR spectra in the type III precursors heat treated at 900°C with that of γ-Al_2O_3[26] suggests that the short-range order of Al-sites in the type III precursors is similar to that in γ-Al_2O_3. Possibly these Al-sites act as γ-Al_2O_3 nuclei above 900°C in the type III precursors. In the case of type I precursors, other mechanisms are activated. Apparently the pentahedral or distorted tetrahedral Al-sites become structurally unstable above ≈900°C. Due to the homogeneous atomic mixture of the Si-, Al- and O-atoms, and the lack of 'γ-Al_2O_3 nuclei' in the type I precursors, mullite formation is the most favourable process energetically (see also Ref. 25).

Schneider *et al.*[14] also described an Al-rearrangement in the precursors prior to crystallization, although it should be kept in mind that their study was not carried out on pure type I and type III precursors but on the combination of both precursors.

The present discussions, based on suggestions made by Sanz *et al.*[25] and on the authors' own data, are in contrast to the reaction processes discussed by Pask & Tomsia.[16] In a review study of the formation of mullite on heating kaolinite and synthetic mixtures of organic starting compounds, Pask & Tomsia[16] related the existence of the exothermic 980°C DTA peak to the mullite formation; accordingly, if no mullite is formed at 980°C, as a consequence no sharp DTA exotherm should appear at this temperature. The observed reaction sequences in the type I and type III samples of this study, however, exclude the assignment of the 980°C exotherm to a particular phase formation.

In the frame of present knowledge, type I precursors transform directly to Al_2O_3-rich mullite, while types II and III and admixtures of various types of precursors transform to mullite in multistep reactions with intermediate formation of γ-Al_2O_3 plus SiO_2. Possibly mullitization in the cases of type II and III is favoured, if only a topotactical transformation of γ-Al_2O_3 into mullite with preservation of Al–O octahedral chains is taken into account (see Ref. 14).

Acknowledgements

The authors wish to thank Dr T. Rymon-Lipinski (Bonn, Germany) for carrying out the DTA studies. H.S., L.M. and A.S. acknowledge the financial support of the Deutsche Forschungsgemeinschaft (DFG, Bonn, Germany). L.M. and A.S. extend their gratitude for the financial support provided by the Fond der Chemischen Industrie (Frankfurt, Germany).

References

1. Aksay, A., Dabbs, D. M. & Sarikaya, M., Mullite for structural, electronic and optical applications. *J. Am. Ceram. Soc.*, **75**(10) (1991) 2343–58.
2. Boch, P., Chartier, T. & Rodrigo, P. D. D., High purity mullite ceramics by reaction-sintering. In *Mullite and Mullite Matrix Composites, Ceramic Transactions*, Vol. 6, ed. S. Somiya, R. F. Davis & J. A. Pask. The American Ceramic Society Inc., Westerville, OH, 1990, pp. 353–74.
3. Hoffman, D. W., Roy, R. & Komarneni, S., Diphasic xerogels, a new class of materials: phases in the Al_2O_3–SiO_2. *J. Am. Ceram. Soc.*, **67**(7) (1984) 468–71.
4. Wheat, T. A., Sallam, E. M. H. & Chaklader, A. C. D., Synthesis of mullite by a freeze-dry process. *Ceram. Int.*, **5**(1) (1979) 42–4.

5. Chakravorty, A. K. & Ghosh, D. K., Synthesis and 980° phase developments of some mullite gels. *J. Am. Ceram. Soc.*, **71**(11) (1988) 978–87.
6. Caldeira, P. A., Correia, R. N. & Baptista, J. K., Characterization, packing and sintering of chemically prepared mullite powders. In *Ceramics Today–Tomorrow's Ceramics—Materials Science Monographs*, Vol. 66B, Part B, ed. P. Vincenzini. Elsevier, Amsterdam, 1991, pp. 871–80.
7. Ossaka, J., Tetragonal mullite-like phase from co-precipitated gels. *Nature* (*London*), **19**(4792) (1961) 1000–1.
8. Horte, H. & Wiegemann, J., Study on the reaction between amorphous SiO_2 and Al_2O_3. *Naturwissenschaften*, **43** (1956) 9–10.
9. Okada, K. & Otsuka, N., Characterization of the spinel phase from SiO_2–Al_2O_3 xerogels and the formation process of mullite. *J. Am. Ceram. Soc.*, **69**(9) (1986) 652–6.
10. Yoldas, B. E., Mullite formation from aluminium and silicon alkoxides. In *Mullite and Mullite Matrix Composites, Ceramic Transactions*, Vol. 6, ed. S. Somiya, R. F. Davis & J. A. Pask. The American Ceramic Society Inc., Westerville, OH, 1990, pp. 255–61.
11. Komarneni, S. & Roy, R., Application of compositionally diphasic xerogels for enhanced densification, the system Al_2O_3–SiO_2. *J. Am. Ceram. Soc.*, **69**(7) (1986) C-155–C-156.
12. Brown, I. W. M., Mackenzie, K. J. D., Bowden, M. E. & Meinhold, R. H., Outstanding problems in the kaolinite–mullite reaction sequence investigated by ^{29}Si and ^{27}Al solid state nuclear resonance: II. High temperature transformations of metakaolinite. *J. Am. Ceram. Soc.*, **68**(6) (1985) 298–301.
13. Low, I. M. & McPherson, R., The origins of mullite formation. *J. Mater. Sci.*, **24** (1986) 926–36.
14. Schneider, H., Merwin, L. & Sebald, A., Mullite formation from non-crystalline precursors. *J. Mater. Sci.*, **27** (1992) 805–12.
15. Kanzaki, S., Tabata, H., Kumazawa, T. & Ohta, S., Sintering and mechanical properties of stoichiometric mullite. *J. Am. Ceram. Soc.*, **68**(1) (1985) C-6–C-7.
16. Pask, J. A. & Tomsia, A. P., Formation of mullite. *J. Am. Ceram. Soc.*, **74**(10) (1991) 2367–73.
17. Okada, K. & Otsuka, N., Formation process of mullite. In *Mullite and Mullite Matrix Composites, Ceramic Transactions*, Vol. 6, ed. S. Somiya, R. F. Davis & J. A. Pask. The American Ceramic Society Inc., Westerville, OH, 1990, pp. 375–87.
18. Iler, R. K., *The Chemistry of Silica*. J. Wiley, New York, 1979, pp. 172–311.
19. Mägi, M., Lippmaa, E., Samoson, A., Engelhardt, G. & Grimmer, A. R., Solid-state high resolution silicon-29 chemical shifts in silicates. *J. Phys. Chem.*, **88** (1984) 1518–22.
20. Engelhardt, G. & Michel, D., *High Resolution Solid-State NMR of Silicates and Zeolites*. Wiley, New York, 1987, pp. 143–57.
21. Colomban, Ph., Protonic defects and crystallization of sol-gel (Si,Ge) mullites and alumina. In *Ceramics Today–Tomorrow's Ceramics—Materials Science Monographs*, Vol. 66B, Part B, ed. P. Vincenzini. Elsevier, Amsterdam, 1991, pp. 599–605.
22. Colomban, Ph. & Mazerolles, L., Nanocomposites in mullite–ZrO_2 and mullite–TiO_2 systems synthesized through alkoxide hydrolysis gel routes: microstructure and fractography. *J. Mater. Sci.*, **26** (1991) 3503–10.
23. Colomban, Ph., Jones, D. J., Grandjean, D. & Flank, A. M., EXAFS and XANES study of (Si,Ge) mullite gels and glasses prepared by slow hydrolysis of alkoxides. Paper presented at 6th International Workshop on Ceramics and Glasses from Gels in Sevilla, Spain, October 1991, to be published in *J. Non-Cryst. Solids.*
24. Smith, J. V. & Blackwell, C. S., Nuclear magnetic resonance of silica polymorphs. *Nature*, **303** (1985) 223–5.
25. Sanz, J., Sobrados, I., Cavalieri, A. L., Pena, P., de Aza, S. & Moya, J. S., Structural changes induced on mullite precursors by thermal treatment: an ^{27}Al MAS NMR investigation. *J. Am. Ceram. Soc.*, **74**(10) (1991) 2398–403.
26. Rocha, J. & Klinowski, J., ^{29}Si and ^{27}Al magic-angle-spinning NMR studies of the thermal transformation of kaolinite. *Phys. Chem. Min.*, **17** (1990) 179–86.