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Influence of Synthesis and Composition on Mullite Crystallization

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Gels with nominal compositions $Al_2O_3 \cdot SiO_2$ and $2Al_2O_3 \cdot SiO_2$ have been prepared using two sol−gel routes, the first one by long gelation time of a solution of TEOS and aluminum nitrate nonahydrate, the second one starting from TEOS and Al alkoxides with different processing conditions. Xerogels with different levels of homogeneity as depicted by their crystallization schemes have been obtained. Whereas mullite with different compositions is obtained after the first 1000 °C exotherm, a similar evolution of the compositions is observed for all samples at higher temperature. The alumina content at 1000 °C has been related to the compositions and relative proportions of local heterogeneities present inside the xerogels.

Introduction

Mullite ($3Al_2O_3 \cdot 2SiO_2$) is a compound of great interest for its applications in electronic, optic, and structural materials. A lot of mullite syntheses have been investigated with different precursors, either soluble precursors such as alkoxides and aluminum nitrate (molecular route) or colloids (colloidal route) as well as mixtures of both kinds of precursors.[1] They have shown the existence of two paths of mullite crystallization during heating:

(1) Direct mullite formation (tetragonal form) from an X-ray amorphous phase at ≈1000 °C. This alumina-rich phase is metastable and progressively reacts with free silica to form orthorhombic mullite.

(2) Indirect mullite formation (orthorhombic form) via an amorphous silica-rich phase and a poorly crystalline high-alumina phase with a spinel structure; this reaction takes then place at ≈1200 °C.

Paths (1) and (2) are observed only for molecular and colloidal precursors respectively, although the second way is sometimes observed with molecular precursors, spinel crystallizing then around 1000 °C from an amorphous phase. The influence of synthesis conditions toward crystallization led authors[2−9] to explain these behaviors in general terms of alumina−silica scale of mixing, or, alternatively, the degree of Al−O−Si bonding in the precursor system. But these concepts failed to explain why gels generally do not crystallize to orthorhombic mullite at temperatures between ≈1000 and ≈1200 °C (whereas a continuous scale of mixing could exist) and why spinel rather than mullite formation is favored (even when comparable precursors were employed).

Hulling and Messing[1] identified the presence of local alumina-rich heterogeneities as being responsible for the preferential spinel formation instead of mullite at 1000 °C. In that case, spinel crystallizes by epitactic nucleation on γ-Al_2O_3 structure of heterogeneities which act as seeds. The role of pentacoordinate aluminum has been proposed[8] to explain the phase evolution at the 980 °C exotherm. Jaymes[10] determined that at this temperature, crystallization of spinel and/or mullite from the amorphous phase is always associated with free silica formation. Moreover, according to the alumina composition of the starting amorphous phase, different crystallization schemes are observed: spinel appears with alumina composition higher than 75 mol %, tetragonal mullite is observed for alumina content lower than 71 mol % and between 71 and 75 mol %, both crystallization paths take place simultaneously, spinel and mullite being observed at 1000 °C. We should also mention that mullite is a solid solution, exhibiting a pseudotetragonal form inside an alumina-rich metastable domain (up to 74 mol %) and an orthorhombic form inside a much restricted stable domain (58.5−62.8 mol %).[11]

The aim of this study is to determine a systematic of crystallization through relations between synthesis−global compositions−homogeneity and mechanisms of crystallization for two compositions inside the Al_2O_3−SiO_2 system on both sides of stoichiometric mullite.

Experimental Section

To obtain a wide range of homogeneity in the gel, two synthesis routes on compositions $Al_2O_3 \cdot SiO_2$ and $2Al_2O_3 \cdot SiO_2$ (noted 1:1 and 2:1, respectively) have been performed.

Synthesis. The first route (also called semi-alkoxide) uses aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, Prolabo, 97%) and tetraethoxysilane (TEOS, Aldrich, 98%) as precursors, as previously described by Hulling and Messing.[1] In this process, hydrolysis is performed by hydration water molecules and the gelation time is around 1 month.

The second route (also called all-alkoxide), involves the use of aluminum and silicon alkoxides as precursors. To decrease its reactivity toward hydrolysis and condensation reactions, aluminum alkoxide is chemically modified with acetylacetone

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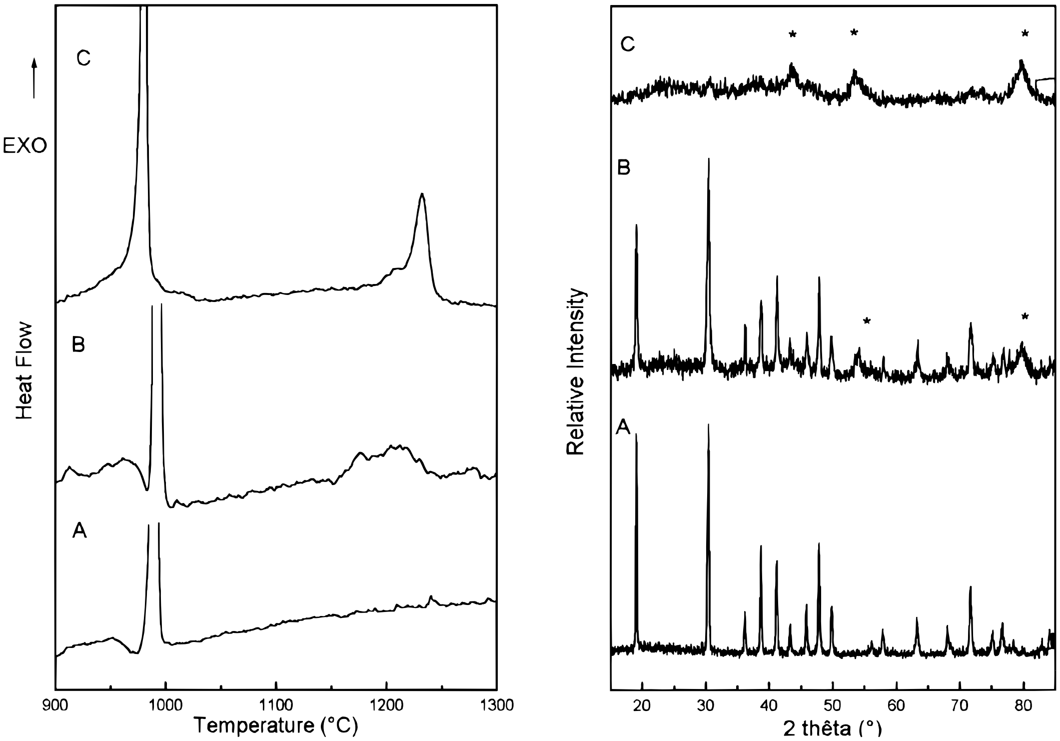

Figure 1. DTA traces (6 °C/min) and X-ray diffraction patterns of three different gels of 2:1 composition. XRD patterns have been recorded on samples previously calcined at 1000 °C. (* is spinel and other lines are mullite).

(acacH) or ethoxyacetylacetone (etacH), according to

$$\mathrm{Al(OR)_3 + ModH \rightarrow Al(OR)_2(Mod) + ROH} \qquad (1)$$

with OR = O^iPr, O^sBu, and ModH = etacH or acacH.

The Mod/Al ratio has been kept equal to 1 for all experiments, higher values promoting the precipitation of $Al(acac)_3$ during the hydrolysis step due to its lower solubility in aqueous medium.

On the other hand, silicon alkoxide can be prehydrolyzed to decrease the difference of reactivity between alkoxides. Reactions take place in 2-propanol (*i*-PrOH) or 2-butanol (s-BuOH) as solvent and hydrolysis are promoted by dropwise addition of a water/alcohol mixture (1/4 proportions) in order to achieve an hydrolysis ratio $h = H_2O/OR = 2$.

In summary, for this second route, four parameters has been considered: (i) aluminum alkoxide OR group; (ii) diketonate ligand; (iii) solvent; (iv) prehydrolysis or not of silicon alkoxide. Gels were dried at 250 °C during 2 h before other thermal treatments.

Characterizations. Differential thermal analysis, DTA (Setaram TGA 92), were performed under air atmosphere on xerogels using a 6 °C/min heating rate. Crystalline phases were identified by X-ray diffraction, XRD (Siemens D500, Co $K\alpha_1$ monochromatized radiation), on samples previously heated just above the relevant exotherms. The mullite alumina content was estimated from the unit-cell parameters using the models of Cameron[12] and Okada.[13] XRD patterns have been recorded for each sample using a step scan procedure with a 0.02° 2θ step and a counting time of 15 s/step. The unit-cell parameters have been refined from these powder data using a nonlinear least-squares program (Eracel) made by Laugier and Filhol (1978).

Results and Discussion

Mechanism of Crystallization. For 2:1 composition, DTA and XRD results (Figure 1) reveal three different behaviors, A, B, and C. For A, only and reproducibly observed for samples obtained using the semi-alkoxide route, only one exotherm is observed at around 995 °C, and it corresponds to the crystallization of pure tetragonal mullite. B and C behaviors are related to samples issued from the all-alkoxide route. Among the different parameters involved for this route, the nature of the solvent seems to have the most important influence since (i) *i*-PrOH promotes in most cases the B behavior and (ii) C behavior is always observed with BuOH as solvent.

For C behavior, two exotherms are detected. The first one between 980 and 1000 °C, according to the processing conditions, corresponds to spinel crystallization, the second one at around 1225−1232 °C, relatively well defined, is associated with the formation of orthorhombic mullite from the spinel phase and an amorphous silica-rich phase. B behavior is a combination of both preceding behaviors with the presence after the first exotherm of a mixture of spinel and tetragonal mullite phases and their evolution into orthorhombic mullite after the second exotherm.

For 1:1 composition, samples issued from a same process than for 2:1 composition have been named A′, B′, and C′ and the corresponding DTA and XRD results are reported in Figure 2. In all cases, only one exotherm is observed corresponding to the crystallization of mullite except for gel C′ where spinel is also detected.

As the preceding experiments give only a picture of the samples just after the relevant exotherms, other thermal treatments have been performed by increasing the annealing temperatures and times.

Evolution of Mullite Composition with Thermal Treatment. For both compositions, three samples characteristic of the A(A′), B(B′), and C(C′) behaviors have been annealed at temperatures ranging from 950 to 1300 °C for 24 h (11 h at 1300 °C). The corresponding compositions of the mullite phases have been determined according to the models of Cameron[12] and

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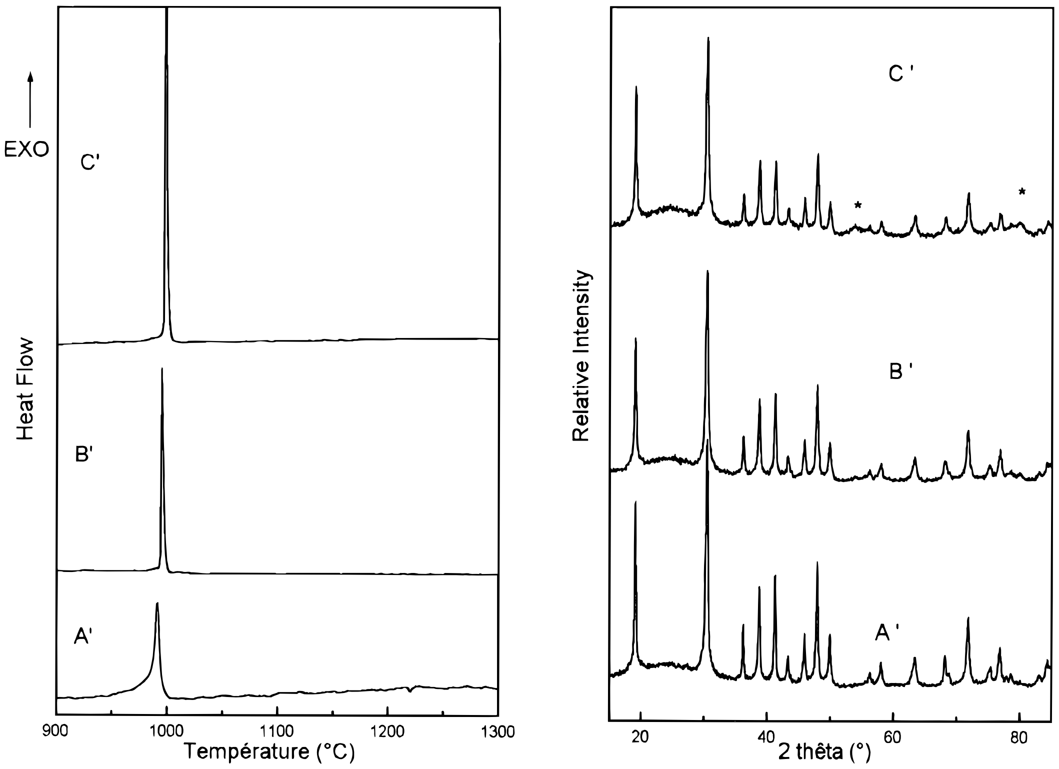

Figure 2. DTA traces (6 °C/min) and X-ray diffraction patterns of three different gels of 1:1 composition. XRD patterns have been recorded on samples previously calcined at 1000 °C. (* is spinel and other lines are mullite).

Table 1. *a* and *b* Cell Parameter Values from XRD Data and Calculated *b* Values

	cell parameters from XRD data (Å)		calculated *b* values (Å)	
	a	*b*	Cameron	Okada
gel A, 1000 °C, 24 h	7.5977(4)	7.6850(3)	7.679	7.689
gel C, 1150 °C, 24 h	7.5753(2)	7.6826(2)	7.686	7.694

Okada.[13] To estimate if our data are consistent with the preceding models, we have compared for two samples the *b* cell parameter values obtained either from powder data refinement or determined using the models from the corresponding a cell parameter value. The results are shown in Table 1 and reveal that Okada's and Cameron's models seem to fit relatively well our *b* value (particularly at the lower temperature). However, as the *b* value evolution is less sensitive to the alumina content, much care has to be taken and we therefore average the alumina contents deduced from both models. The resulting values are reported in Table 2.

Evolution with Temperature. Increasing the temperature of thermal treatment promotes a decrease of Al_2O_3 content in mullite in relation with a progressive transformation from tetragonal to orthorhombic mullite. For the highest temperature (1300 °C), the α-Al_2O_3 phase is detected for 2:1 samples.

Composition of Mullite at the Crystallization Temperature. Long treatment at low temperature (950 °C, 24 h) allows us to crystallize mullite with the highest alumina contents, ranging from 67.6 to 71.2 mol %, except gel C which yields the crystallization of spinel phase. Surprisingly, the alumina contents of samples with 1:1 starting composition appear of the same order or even higher than those of 2:1 composition.

Discussion

It appears from the experimental results that three crystallization mechanisms, A, B, and C, are evidenced in the case of 2:1 composition. This means that the modification of elaboration conditions yields gels with different homogeneity levels. If the same experimental conditions are duplicated for 1:1 composition, the samples are much more similar to each other with the presence of only one exotherm. Therefore, the starting composition also plays a role in further evolution of the gels. The discussion tries to take account of both parameters: homogeneity in relation with processing conditions and role of composition.

For 2:1 composition, at around 1000 °C, pure tetragonal mullite form is achieved only for gel of the semi-alkoxide route (type A) whereas spinel is obtained only from gels of the all-alkoxide route (types B and C). This observation implies that all-alkoxide route leads to local alumina-rich heterogeneities. It can probably be related with the difference of reactivity in the dual alkoxide system. However, one has to remember that the formation of spinel from an all-alkoxide route can be avoided by using a much more controlled process as shown by Yoldas.[6] This problem seems to be not encountered with the semi-alkoxide route, again keeping in mind that very slow gelation conditions have been adopted.[1,4] As far as the second exotherm is concerned, differences between B and C behaviors are attributed to the presence, in the first case, of mullite at 1000 °C. This phase acts as nucleating seeds[1] and decreases the temperature of mullitization of gel B. Moreover, its presence indicates, a posteriori, a better homogeneity (or a lower content of alumina-rich heterogeneities) than for gel C. The fact that the DTA peak becomes broader could be characteristic of a more progressive reaction in relation with the presence of mullite seeds.

Table 2. Alumina Contents for Different Samples According to Their Thermal Treatment[a]

thermal treatment	A	B	C	A′	B′	C′
950 °C, 24 h	70.2(10)	67.6(10)	Sp	68.0(8)	71.2(11)	69.0(9)
1000 °C, 24 h	69.0(8)	67.7(7)	Sp	66.1(7)	69.2(10)	69.8(10)
1100 °C, 24 h	68.7(8)	66.2(5)	Sp	nm	nm	nm
1150 °C, 24 h	67.3(7)	65.4(5)	66.1(6)	62.4(2)	62.4(2)	64.6(4)
1200 °C, 24 h	66.3(5)	64.6(4)	65.3(5)	nm	nm	nm
1300 °C	65.6(5)	63.2(2)	65.1(5)	59.4(2)	58.8(3)	58.8(3)

[a] Sp: only spinel phase is detected; nm: not measured.

For 1:1 composition, the decrease of alumina content compared to 2:1 composition promotes the crystallization of mullite instead of spinel. This observation could be related to the fact that decreasing the alumina proportion will induce, for the same process, a lower probability to form local alumina-rich heterogeneities. From a more general point of view, it can be considered as a "dilution" effect, SiO_2 being the "solvent".

In all cases, a decrease of alumina content in mullite with increasing temperature is observed and two phenomenas could be invoked:

(1) Incorporation of free silica formed during the crystallization of alumina-rich phase(s) at ≈1000 °C (tetragonal mullite and/or spinel). It will continue until complete silica incorporation (2:1 composition) or until the silica-rich limit of the mullite solid solution is reached (around 58−59 mol % alumina for 1:1 composition).

(2) Decomposition of 2:1 metastable mullite phases at high temperature. All free silica is consumed at around 1150−1200 °C as revealed by the alumina contents (Table 2) deduced from the *a* cell parameter values giving rise to mullite with nominal composition. This composition corresponds to a metastable phase[11,14] that decomposes progressively to more stable mullite (lower alumina content) and α-Al_2O_3 as detected by X-ray diffraction at higher temperature (1300 °C).[15]

Further consideration of the results presented in Table 2 reveals an evolution not only vertically, i.e., versus temperature, but also horizontally, i.e., versus process and composition. However, some care must be taken since, for some samples, the differences between corresponding values are of the same order as the incertitudes. To try to explain the differences in composition between samples A, B, C, A′, B′, and C′, some previously reported results must be remembered. Crystallization of alumina-rich phases (spinel or mullite) at 1000 °C is associated with the formation of amorphous silica. Therefore, the composition of the crystalline phase is richer in alumina than the amorphous phase where it comes from. The determination of mullite composition gives indications concerning the composition of the amorphous phase that crystallizes: this last one has an alumina content lower than mullite. Moreover, as suggested by many authors,[10,16] the devitrification of an aluminosilicate amorphous phase is easier when alumina composition increases. We should then postulate that the richest alumina heterogeneities crystallize first and that they determine the crystallization mechanism and mullite composition.

The following considerations are proposed to explain the results presented in Table 2:

(1) Comparison of gels A and B shows the formation of mullite with a lower alumina content for gel B than for gel A. It could be attributed to the concomitant presence of spinel for gel B. This last phase crystallizes from heterogeneities which alumina content is higher than 75 mol % and its growth, faster than mullite,[1] probably consumes alumina to the detriment of mullite. The same observation can be done between gels B′ and C′.

(2) Although pure tetragonal mullite is obtained for gel A′, its alumina content is lower than that of gel C′, which also contains spinel, in contradiction with the preceding explanation. This phenomenon is probably in relation to the better homogeneity of gel A′ due to its semi-alkoxide synthesis route. For 2:1 composition, only this route yields the formation of pure mullite. Therefore, the better homogeneity attained by the semi-alkoxide route implies that the places where crystallization is induced have a composition closer to the nominal one, i.e., a lower alumina content.

(3) The previous considerations are confirmed for samples with different nominal compositions such as A′ and B′ (pure mullite) and B (mullite + spinel). The first ones yield a mullite with a higher alumina content than for gel B in relation with the absence of spinel phase although their nominal alumina contents are lower than for gel B.

(4) For pure tetragonal mullite samples, the alumina content of corresponding mullite phases follows the sequence B′ > A > A′. It seems to evidence that the most determining factor for determining the mullite composition is not the global composition but rather the composition of local heterogeneities that is governed by the type of synthesis.

Conclusion

By varying the starting composition, 2:1 and 1:1, and the synthesis conditions, semi-alkoxide and all-alkoxide, samples with different crystallization behaviors have been obtained in the Al_2O_3−SiO_2 system. The crystallization schemes have been related to the presence of local heterogeneities as previously depicted by Hulling and Messing.[1] Their compositions and relative proportions will influence the evolution of the sample at the temperature of the first exotherm (around 1000 °C). If the local composition of the heterogeneities does not exceed 71% Al_2O_3, crystallization of tetragonal mullite takes place at the first exotherm (sample A). On the contrary, presence of heterogeneities with an Al_2O_3 content higher than 75% will promote exclusive crystallization of spinel (sample C). For an intermediate distribution (sample B), both phases will be observed, spinel crystallization inducing the formation of tetragonal mullite with a lower Al_2O_3 content compared to sample A.

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