

# Mullite Formation from Highly Homogeneous Mixtures of $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$

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**Abstract**—Mullite,  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , was synthesized by heat-treating homogeneous sol–gel-derived mixtures of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  taken in stoichiometric amounts. To reduce the mullitization temperature, sols containing  $\gamma\text{-AlOOH}$  and  $\text{SiO}_2$  nanoparticles (2 to 20 nm) were used in the preparation of the mullite precursors. A few samples were made using the products of hydrolysis of aluminum salts instead of the  $\gamma\text{-AlOOH}$  sol. The process parameters determining the homogeneity of the precursor mixtures were revealed. The preparation conditions ensuring mullite crystallization at temperatures between 1200 and 1250°C were found. The results are discussed in terms of the reaction between  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  during mullitization.

## INTRODUCTION

Mullite ceramics are noted for their low thermal-expansion coefficient (mean value is  $5.0 \times 10^{-6} \text{ K}^{-1}$ ) and high heat resistance, flexural strength (150 MPa at  $\approx 1400^\circ\text{C}$ ), creep resistance, and durability in acidic media [1, 2]. However, these parameters are characteristic of pure, well-sintered, single-phase materials only. The manufacturing technology has a strong effect on the properties of mullite. Conventional solid-phase sintering of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  requires considerable effort and time [2]. In recent years, the progress in sol–gel processing, which makes it possible to decrease the temperatures of solid-state transformations, has stimulated intense interest in mullite [3].

According to the type of mullite precursors, the approaches to sol–gel mullite processing can be divided into three groups: (1) Procedures yielding single-phase gels, in which a polymeric  $-\text{Al}-\text{O}-\text{Si}-$  network is formed through hydrolysis of aluminum and silicon alkoxides, ensuring molecular-scale mixing of alumina and silica [4, 5]; (2) colloidal techniques, involving nanometer-scale (1 to 100 nm) mixing of appropriate sols to give diphasic gels—colloidal mixtures of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  [1, 3, 6]; (3) combined approach, involving the mixing of polymerically and colloidally derived sols to give hybrid gels in which the scale of mixing is intermediate between those of the first two processes [7].

The type of mullite precursor determines the sequence of phase transformations and their tempera-

tures during heat treatment. Mullitization of polymeric and colloidal gels takes place at about 980°C and 1250–1350°C, respectively. Mullite formation through a solid-state reaction between fine (1–2  $\mu\text{m}$ )  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  powders occurs at temperatures above 1600°C [2, 8]. Thus, improving the homogeneity of the mixture reduces the mullitization temperature. This might be expected to predetermine the type of mullite precursor and the preparation procedure. However, the preparation of polymeric gels from aluminum and silicon alkoxides is impaired by the high cost of the starting materials and difficulties in process control, which makes colloidal techniques more attractive [1].

One of the challenges in the preparation and heat treatment of colloidal gels is to bring the conditions of mullite formation closer to those characteristic of polymeric gels [1]. A major parameter of the process is the mullitization temperature, determined mainly by the homogeneity of the starting material. In this work, we aimed at improving the homogeneity of  $\text{Al}_2\text{O}_3 + \text{SiO}_2$  mixtures in mullite precursors by using nanoparticle (2–20 nm) sols or the products of hydrolysis of aluminum salts in the liquid phase of the  $\text{SiO}_2$  sol.

## EXPERIMENTAL

$\text{SiO}_2$  sols were prepared by ion exchange. To prepare  $\text{SiO}_2$  sols containing larger particles, we used the technique reported in [9]. The sols contained 3 wt %  $\text{SiO}_2$  (pH 2.8). The second component was pseudoboehmite ( $\gamma\text{-AlOOH}$ ), precipitated from an aqueous solu-

tion of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  heated to just below the boiling point and adjusted to pH 7–8 with concentrated aqueous ammonia. The precipitate was washed with distilled water and dried at 80 or 120°C. The dried material was peptized with  $\text{HNO}_3$  at an  $\text{NO}_3/\text{Al}$  molar ratio  $\beta = 0.07$  or 0.33. The solids loading of the  $\gamma\text{-AlOOH}$  sol was 3 wt %. The silica and pseudoboehmite sols were mixed to give the mullite stoichiometry. A number of samples were prepared using, instead of the  $\gamma\text{-AlOOH}$  sol, the products of hydrolysis of aluminum salts in the liquid phase of the silica sol.

The particle size of the sols was determined using an MOM-3180 ultracentrifuge (Hungary). Selected sols were examined by transmission electron microscopy (TEM) with a JEM-200CX microscope operating at 200 kV.

Differential thermal analysis (DTA) was carried out at a heating rate of 10°C/min in the temperature range from 20 to 1500°C using a DTA TYP701 thermal analyzer (Baehr, Germany). The phase composition of the reaction products was analyzed by x-ray diffraction using a Philips powder diffraction system equipped with a PW 1050/80 goniometer and a PW 170 microprocessor system. In quantitative phase analysis, we used the QUAN1877 program (E. Halwax, 1994). Mullite,  $\gamma\text{-Al}_2\text{O}_3$ ,  $\delta\text{-Al}_2\text{O}_3$ , and  $\alpha\text{-Al}_2\text{O}_3$  were used as calibration standards.

Isothermal heat treatment of the samples was performed in an AHTL 201400 high-temperature furnace (Austria) at 1000, 1200, and 1250°C. The heating rate was 10°C/min.

## EXPERIMENTAL RESULTS

In assessing the effect which the particle size of alumina and silica sols, varied from 2 to 20 nm, has on

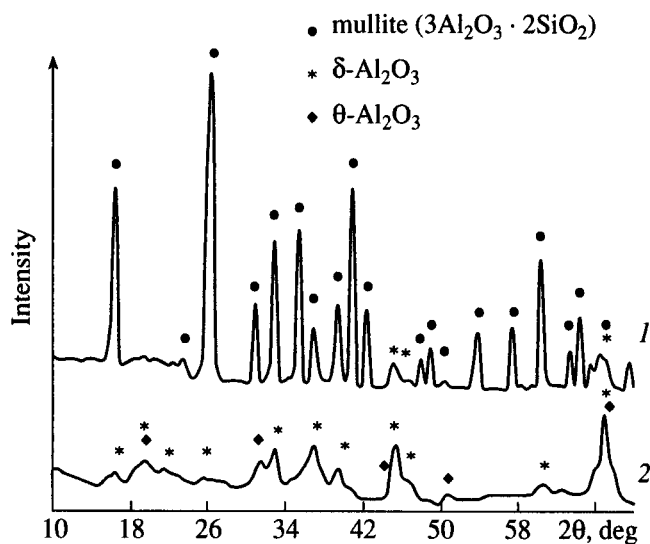


Fig 1. X-ray diffraction patterns of samples (1) M1 and (2) M2 heat-treated at 1200°C for 1 h.

mullite formation during heat treatment of the resulting gels, we took into account that, under certain conditions, a decrease in particle size can lead to interaction between particles of the same type, resulting in  $\text{Al}_2\text{O}_3\text{-Al}_2\text{O}_3$  and  $\text{SiO}_2\text{-SiO}_2$  aggregation effects. The resultant inhomogeneity of the oxide mixture may impede the reaction between  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  and, consequently, mullite formation. Our experiments made it possible to assess the effect of this parameter on the subsequent phase transformations. Experimental conditions were chosen so as to increase the area of the  $\text{Al}_2\text{O}_3\text{-SiO}_2$  interface, which plays an important part in mullite nucleation.

Our results are summarized in the table. Sample M1, prepared by mixing freshly prepared  $\gamma\text{-AlOOH}$  and  $\text{SiO}_2$  sols (aging times  $\tau_1 = \tau_2 = 0$ ), was chosen as a control. The silica sol was made by dispersing  $\text{SiO}_2$  powder with a particle diameter  $d_1 = 2 \pm 0.5$  nm in a pH 2.8 solution. The  $\gamma\text{-AlOOH}$  sol had the following characteristics: temperature of pseudoboehmite drying  $t = 80^\circ\text{C}$ ,  $\text{NO}_3/\text{Al}$  molar ratio during peptization of  $\gamma\text{-AlOOH}$   $\beta = 0.33$ , and particle size  $d_2 = 6 \pm 2$  nm. For the other samples, the preparation conditions differing from those of the control sample are listed in the table. Each of the samples was heat-treated at 1000, 1200, and 1250°C for 24, 1, and 1 h, respectively. The diffraction patterns of samples M1 and M2 (1200°C), differing markedly in phase composition, are shown in Fig. 1.  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  and  $\delta\text{-Al}_2\text{O}_3$  are easy to identify in diffraction patterns.  $\delta\text{-Al}_2\text{O}_3$  and  $\theta\text{-Al}_2\text{O}_3$  are more difficult to distinguish from one another; however, the former phase typically dominates over the latter.

The preparation conditions were varied so as to highlight the effect of particular characteristics of the sols or their mixtures on mullite formation. For instance, conditions favorable for particle aggregation in the silica sol before mixing with the  $\gamma\text{-AlOOH}$  sol were provided in the preparation of samples M3 and M4. In preparing M3, the pH of the silica sol was raised to 5.5 by adding aqueous ammonia, in order for the sol to become colloiddally unstable [10], and the sol was held for 40 min before mixing. The TEM image of sample M3 (Fig. 2a) confirms the formation of  $\text{SiO}_2$  aggregates on the order of 100 nm in size. In the preparation of M4, the pH of the silica sol was 2.8, but the sol was aged for 7 days. In both cases, the aging time was equal to half the gelation time.

The procedure for preparing sample M5 was elaborated taking into account several factors.  $\text{SiO}_2$  and  $\gamma\text{-AlOOH}$  particles may undergo heterocoagulation. In the pH range from 5 to 6, their zeta potentials differ in magnitude most significantly and are opposite in sign [11]. Upon mixing the  $\text{SiO}_2$  (pH 8.0) and  $\gamma\text{-AlOOH}$  (pH 3.2) sols, the mixture gains a pH value favorable for heterocoagulation. On the one hand, heterocoagulation should result in good mixing of  $\text{SiO}_2$  and  $\gamma\text{-AlOOH}$  particles. On the other, the formation of  $\text{SiO}_2\text{-SiO}_2$  aggreg-

Preparation conditions for Al<sub>2</sub>O<sub>3</sub> + SiO<sub>2</sub> mixtures and phase composition of the heat-treated materials

Sample no.	Preparation conditions*	Phase composition (wt %) after heat treatment	
		1200°C	1250°C
M1	SiO <sub>2</sub> sol: $d_1 = 2$ nm, pH 2.8, $\tau_1 = 0$ ; $\gamma$ -AlOOH sol: $t = 80^\circ\text{C}$ , $\beta = 0.33$ , $d_2 = 6$ nm, $\tau_2 = 0$	Mullite, 70 $\delta$ -Al <sub>2</sub> O <sub>3</sub> , 30	Mullite, 100
M2	SiO <sub>2</sub> sol: $d_1 = 20$ nm	$\delta$ -Al <sub>2</sub> O <sub>3</sub> + $\theta$ -Al <sub>2</sub> O <sub>3</sub> , 100	Mullite, 84 $\theta$ -Al <sub>2</sub> O <sub>3</sub> , 16
M3	SiO <sub>2</sub> sol: $\tau_1 = 40$ min, pH 5.5	Mullite, 23 $\delta$ -Al <sub>2</sub> O <sub>3</sub> , 77	Mullite, 100
M4	SiO <sub>2</sub> sol: $\tau_1 = 7$ days, pH 2.8	Mullite, 32 $\delta$ -Al <sub>2</sub> O <sub>3</sub> , 68	Mullite, 100
M5	SiO <sub>2</sub> sol: pH 8.0	Mullite, 16 $\delta$ -Al <sub>2</sub> O <sub>3</sub> , 84	Mullite, 100
M6	$\gamma$ -AlOOH sol: $t = 120^\circ\text{C}$	Mullite, 34 $\delta$ -Al <sub>2</sub> O <sub>3</sub> , 66	Mullite, 100
M7	$\gamma$ -AlOOH sol: $\beta = 0.07$	Mullite, 70 $\delta$ -Al <sub>2</sub> O <sub>3</sub> , 30	Mullite, 100
M8	$\gamma$ -AlOOH sol: $\tau_2 = 4$ h	Mullite, 20 $\delta$ -Al <sub>2</sub> O <sub>3</sub> , 80	Mullite, 100
M9	Al-containing component introduced into the SiO <sub>2</sub> sol as Al(CH <sub>3</sub> COO) <sub>3</sub> , then hydrolyzed, and precipitated by (CH <sub>2</sub> ) <sub>6</sub> N <sub>4</sub>	Mullite**, 26 $\delta$ -Al <sub>2</sub> O <sub>3</sub> , 74	Mullite, 51 $\delta$ -Al <sub>2</sub> O <sub>3</sub> , 49
M10	SiO <sub>2</sub> sol: $d_1 = 20$ nm; Al-containing component prepared by the same procedure as for M9	Mullite, 55 $\delta$ -Al <sub>2</sub> O <sub>3</sub> , 45	Mullite, 64 $\delta$ -Al <sub>2</sub> O <sub>3</sub> , 36
M11	SiO <sub>2</sub> sol: $d_1 = 20$ nm; Al-containing component prepared by a procedure analogous to M9 but with the use of Al(NO <sub>3</sub> ) <sub>3</sub>	Mullite, 13 $\delta$ -Al <sub>2</sub> O <sub>3</sub> , 87	Mullite, 62 $\delta$ -Al <sub>2</sub> O <sub>3</sub> , 38

\* We give only the preparation conditions differing from those of M1.

\*\* Mullite was found to form at 1000°C.

gates is also possible. As pH is raised from 2.8 to 8.0, the silica sol becomes highly unstable and irreversible particle aggregation takes place [10]. On the whole, one might expect intimate contact between SiO<sub>2</sub> and  $\gamma$ -AlOOH particles owing to heterocoagulation and, at the same time, the formation of an inhomogeneous mixture owing to SiO<sub>2</sub>-SiO<sub>2</sub> aggregation.

Samples M6-M8 were prepared using  $\gamma$ -AlOOH sols with different parameters. If pseudoboehmite was dried at 80°C and peptized at  $\beta = 0.33$  (sample M1), we obtained near-spherical sol particles  $6 \pm 2$  nm in diameter. Drying pseudoboehmite at 120°C (sample M6) resulted in larger-sized, elongated particles (Fig. 2b) [12]. Probably, the concentration of terminal OH-groups decreased owing to olation and oxolation, which are known to reduce the surface activity of  $\gamma$ -AlOOH particles.

Decreasing  $\beta$  to 0.07 (sample M7) leads to a pseudoboehmite sol containing coarser particles (Fig. 2c) in comparison with sample M1, prepared at  $\beta = 0.33$ . Increasing the particle size of the sol decreases the probability of aggregation, which is favorable for the homogeneity of the oxide mixture.

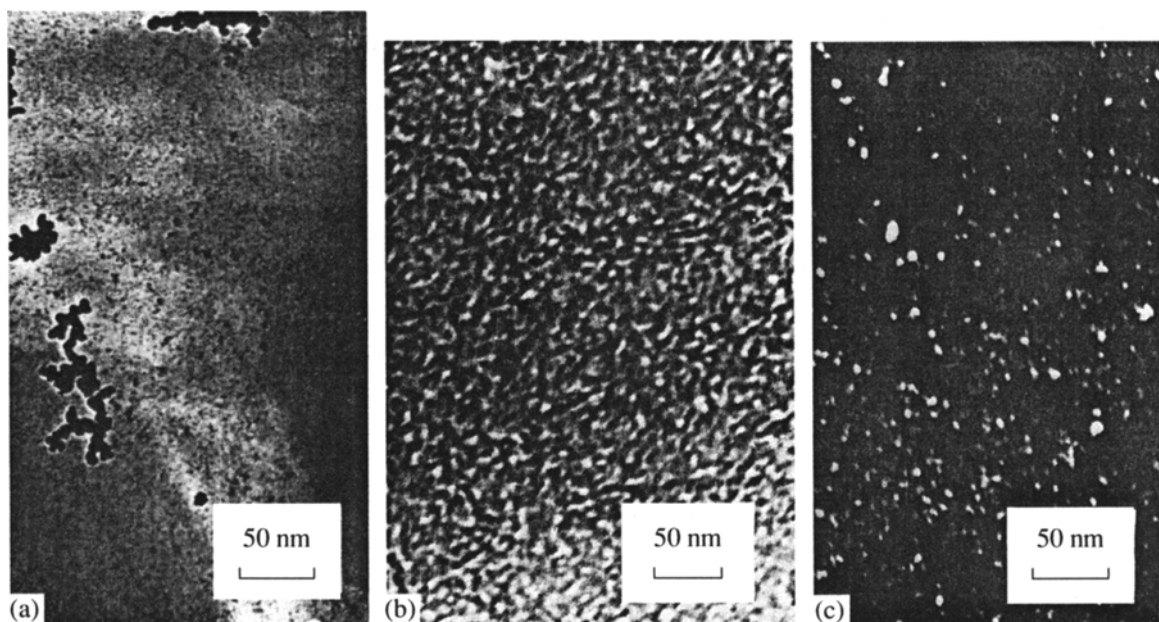
The aggregation of  $\gamma$ -AlOOH particles was promoted in the case of sample M8. For this purpose, the

$\gamma$ -AlOOH sol was aged for 4 h before mixing. The observed increase in the viscosity of the sol indicated particle aggregation.

Difficulties are encountered not only in the preparation of homogeneous colloidal gels from Al- and Si-containing constituents but also with polymeric gels. As shown earlier [13], the homogeneity of the Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>-Al(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O system can be improved by hydrolyzing the aluminum salt in the presence of NH<sub>3</sub> forming via urea decomposition. In a similar way, we precipitated aluminum hydroxide by adding (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub> to Al(CH<sub>3</sub>COO)<sub>3</sub> + SiO<sub>2</sub> or Al(NO<sub>3</sub>)<sub>3</sub> + SiO<sub>2</sub> mixtures. The silica sols contained particles measuring 2 (M9) or 20 nm (M10, M11) in size.

## DISCUSSION

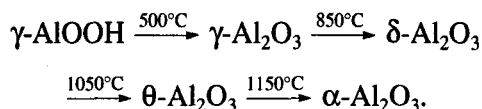
The present results can be interpreted in terms of the interaction between Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> nanoparticles during heat treatment. Various mechanisms of mullite formation from colloidal mixtures have been proposed in the literature [3, 7, 8, 14, 15]. We rely on the model which assumes that mullite nucleates at the Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> interface [1, 14]. This model considers homogeneous mixtures of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> with a large interfacial



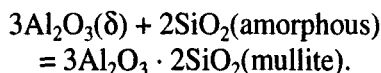
**Fig. 2.** TEM images of the (a)  $\text{SiO}_2$  sol aged at pH 5.5 for 40 min, (b)  $\gamma\text{-AlOOH}$  sol prepared from pseudoboehmite dried at  $120^\circ\text{C}$ , and (c)  $\gamma\text{-AlOOH}$  sol peptized with  $\text{HNO}_3$  at  $\beta = 0.07$ .

area—conditions crucial for mullite crystallization between  $1000$  and  $1200^\circ\text{C}$ .

$\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  react to yield mullite at temperatures above  $900^\circ\text{C}$ , and both undergo a sequence of phase transformations during heating to the mullitization temperature. Heating  $\gamma\text{-AlOOH}$  leads to the following transformations [6]:



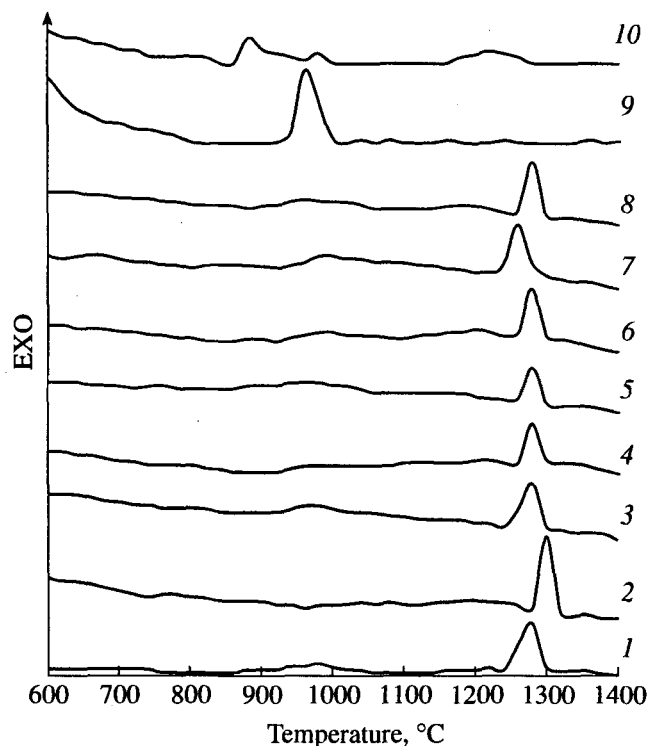
Amorphous silica is rather stable to crystallization: cristobalite is formed at  $t \geq 1200^\circ\text{C}$  [6]. Our results indicate that mullite formation is preceded by the formation of  $\delta\text{-Al}_2\text{O}_3$ . As evidenced by the exothermic peak in the DTA curve (Fig. 3),  $\delta\text{-Al}_2\text{O}_3$  crystallizes between  $960$  and  $1000^\circ\text{C}$  (to reveal this event, the heating rate was reduced). Therefore, in the samples studied, mullite is formed by the following reaction:



Mullite nucleates at the  $\text{Al}_2\text{O}_3\text{-SiO}_2$  interface; therefore, the larger the interfacial area, the higher the probability of nucleation. The most favorable conditions were provided in sample M9, where silica particles were covered with the products of hydrolysis of the aluminum salt. Indeed, this sample was found to contain mullite after 24 h of heat treatment at  $1000^\circ\text{C}$ , which is close to the mullitization temperature of polymeric gels [7, 8]. Nevertheless, we ascribe the exotherm at  $944\text{--}986^\circ\text{C}$  to the crystallization of  $\delta\text{-Al}_2\text{O}_3$  (Fig. 3). This

event is well pronounced since the  $\text{Al}_2\text{O}_3$  in sample M9 remains x-ray amorphous up to these temperatures.

The interfacial area in the samples prepared by mixing  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  sols is rather large; therefore, the



**Fig. 3.** DTA curves of samples (1) M1, (2) M2, (3) M3, (4) M4, (5) M5, (6) M6, (7) M7, (8) M8, (9) M9, and (10) M10.

probability of mullite nucleation is also high. As evidenced by DTA data, mullitization in these samples starts at 1150–1240°C (Fig. 3). In sample M2, prepared with the use of a silica sol containing 20-nm particles, mullitization proceeds at higher temperatures, since the  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  interfacial area is smaller as compared to that of the samples containing smaller particles.

At  $t \geq 1200^\circ\text{C}$ , the mullite yield is low because of the low rate of the diffusion processes involved. At higher temperatures, the diffusivity of the ions increases and the region of mullite formation expands. However, increasing the particle size of  $\text{SiO}_2$  to about 20 nm (sample M2) decreases the mullite yield both at 1200 and 1250°C (table). At the heating rate used in our DTA studies, mullitization occurs at a higher temperature of 1260–1280°C (Fig. 3) and homogeneity is of no significance for most of the samples. However, the DTA peak related to the mullitization of sample M2 is shifted to 1308°C.

According to TEM data, the size of mullite crystallites in our samples is as large as 200 nm. This indicates that precursor regions of approximately the same size are homogeneous and contain stoichiometric amounts of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . Inhomogeneities on the same scale arise because of the  $\text{SiO}_2$ - $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$  aggregation effects. For this reason, the mullite yield for samples M3–M5, M8, and M9 is low at 1200°C (table). At 1250°C, the yield increases for all samples except M9. The mullite yield for sample M10 is slightly higher than that for M9, since 20-nm  $\text{SiO}_2$  particles penetrate more easily into  $\text{Al}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$  aggregates than do 2-nm particles, which accumulate near the surface of the aggregates, affecting the mixture homogeneity.

Not only the preparation procedure but also the nature of the starting reagents have a significant effect on mullite formation. The use of  $\text{Al}(\text{NO}_3)_3$  instead of  $\text{Al}(\text{CH}_3\text{COO})_3$  considerably decreases the mullite yield at 1200°C (sample M11). This indicates a higher degree of aggregation of aluminum hydroxide particles, which decreases their reactivity.

## CONCLUSION

Decreasing the particle size of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  sols to  $2 \pm 0.5$  and  $6 \pm 2$  nm, respectively, reduces the mullitization temperature of their mixture: partial mullitization takes place at 1200°C, and full conversion is achieved at 1250°C in 1 h. With ordinary reagents, mullite forms at 1300°C in 2 h [1]. Various factors influence the scale of  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  mixing and, consequently, the mullite yield at relatively low temperatures ( $\leq 1200^\circ\text{C}$ ). The most favorable conditions for 1200°C mullitization are achieved in homogeneous mixtures of  $\gamma$ - $\text{AlOOH}$  and  $\text{SiO}_2$  sols with a large interfacial area. The best results were obtained with the mullite precursor made by mixing freshly prepared 2-nm  $\text{SiO}_2$  and 6-nm

$\gamma$ - $\text{AlOOH}$  sols, the latter prepared by peptizing pseudo-boehmite dried at 80°C.

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