Mullite (3Al₂O₃–2SiO₂) Synthesis with Aluminosiloxanes

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High-yield mullite (3Al₂O₃–2SiO₂) precursors consist of aluminosiloxanes synthesized from mixtures of aluminum and silicon alkoxides. Atomic level mixing of the aluminum and silicon oxides is demonstrated by the low-temperature conversion (<1000 °C) of the aluminosiloxanes to phase-pure mullite. The proper selection of monomeric side groups serves several functions: (i) controlling reactivity of the silicon and aluminum monomers, thereby favoring atomic-level mixing; (ii) maintaining the tractability of the resulting aluminosiloxane; (iii) improving the yield during mullitization of the aluminosiloxane through easy thermolytic removal. The tractability of the aluminosiloxane compounds permits these materials to be used in fiber spinning, the casting of thin films and monoliths, and as impregnants to powder compacts.

Introduction

Interest in mullite (3Al₂O₃–2SiO₂) spans a wide range of technologies due to its unique thermal, chemical, dielectric, and optical properties.[1–7] The type of precursors used for the synthesis and processing of mullite plays a key role on the shape-forming characteristics, sinterability, and the final properties of the product. While particulate or macromolecular colloids are preferred in fiber processing, powders are the most common form used in the fabrication of bulk objects. In all cases, the spatial scale at which the components (e.g., aluminum and silicon oxides or their precursors) are mixed determines the reaction sequence leading to the formation of mullite. Mixing at the atomic scale is useful for producing mullite at temperatures below 1000 °C; however, powders produced by this approach do not easily sinter and temperatures higher than 1500 °C are required for full densification. Precursors composed of segregated phases are better suited for low temperature densification (1250–1500 °C) due to the formation of a silica-rich viscous phase that aids densification. This phase segregation is usually retained to some degree in the final product, which will contain amorphous inclusions that deleteriously affect mechanical and optical properties.[1]

In this study, we sought to synthesize mullite from *tractable* aluminosiloxanes mixed at the atomic scale.

Prior studies have shown that these precursors can yield phase-pure mullite at temperatures below 1000 °C and are suitable for fiber spinning or film-forming applications.[8–10] Our specific goal was to increase the conversion yields of the precursors to mullite to minimize cracking due to excessive shrinkage and thus to expand the range of applications to include the processing of bulk shapes. The precursors that we have synthesized have been shown to maintain chemical homogeneity throughout mullitization, evidenced by the low temperature of conversion (∼980 °C), and to completely convert to mullite. The precursors remain tractable due to the presence of stable organic side groups and can be used in forming tapes, fibers, and coatings of extremely high purity and as effective impregnants to porous powder compacts.

The methods for synthesizing high-purity mullite range across several length scales, with shorter scales indicating higher precursor homogeneity. At the macroscopic end of the range (∼μm scale), mixtures of colloidal powders (e.g., aluminosilicate clays mixed with alumina powders) are reaction sintered to form mullite.[1,2,11] In these systems, the scale of homogeneity is set by the size of the component powders, and mullitization is delayed to high temperatures (>1650 °C). Mullitization on this length scale proceeds by reaction at the interface between the respective phases.[1,2]

Near atomic scale mixing has used metal salts and/or metal alkoxides to prepare homogeneous precursors at the nanometer scale.[12–24] Small-scale mullitization is driven by the diffusion of the aluminum moiety into

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Table 1. Aluminum and Silicon Monomers Used in This Study (Schematic Structures of the Monomeric Units Shown in Figure 1)

aluminum-only monomers	silicon-only monomers	silicon−aluminum monomer
aluminum diisopropoxide acetoacetic ester chelate aluminum tri-*sec*-butoxide aluminum triisopropoxide	diphenylsilanediol octamethylcyclotetrasiloxane dimethyldiacetoxysilane tetramethylcyclotetrasiloxane	dibutoxyaluminoxytriethoxysilane

a siliceous matrix until the critical concentration required for mullite nucleation is achieved. The transformation of a molecularly homogeneous precursor is signaled by an exothermic reaction at ∼980 °C.[22,23] It has been shown that mullitization, spinel formation, and silica segregation can occur simultaneously at 980 °C, with mullitization favored over spinel formation as the degree of homogeneity increases (also marked by a reduced temperature of mullitization).[25,26] Although extremely slow hydrolysis (≥4 weeks[19]) of a sol−gel mixture results in a viscous precursor with short diffusional lengths,[19,22,25,26] phase segregation remains a significant problem as the control parameters, pH, and ambient conditions, while effective, require long processing times (up to several weeks) and the exclusion of excessive water for the synthesis of homogeneous materials.[27] Even slight inheterogeneities in the structure of precursors that otherwise appear to be homogeneous at longer length scales are sufficient to cause phase separation within the precursor at temperatures near 980 °C.[14,23,28]

Many sol−gels are not atomically homogeneous because the base structure is that of a collection of clusters composed of substituted macromolecular alumoxanes, in which silicon is segregated to the pendant groups around an alumoxane core.[29,30] The core consists of fused Al₂O₂ rings, analogous in structure to the aluminum-centered octahedron found in boehmite and diaspore, encapsulated by terminal triethylsiloxyl (≡O−SiEt₃) groups.[29] If sufficient care is taken, the size of the alumina core can be reduced, lowering the diffusional length scale and enhancing mullitization. Also, segregation can be avoided by synthesizing an aluminosiloxane with the appropriate stoichiometry as a precursor to mullite, putting the scale of homogeneity at the atomic level.[8−10,28−31] A polymeric structure consisting of alternating alumoxane and siloxane groups
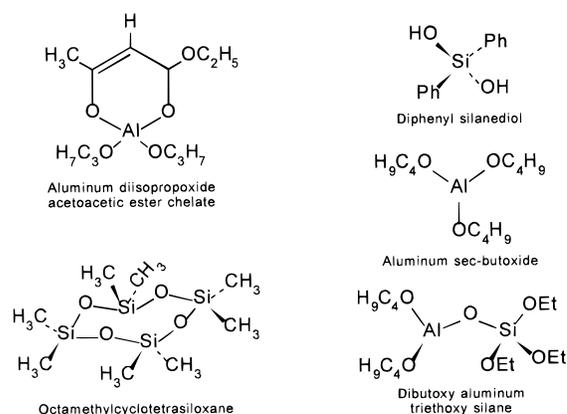
Figure 1. Monomeric schematics of the chemicals used in this study.

would represent an ideal arrangement for a mullite precursor. Molecular weights and the tractability of such a macromolecule can be controlled by controlling the nature of the side chains and/or the chemistry of the solvent carrier.[10,28] By controlling viscosity, spinnable solutions have been used to prepare dense fibers,[10] but the low conversion yields of these systems (<35% ceramic yield)[8−10] limit application to the fabrication of films or bulk monoliths, where the large material losses during conversion would result in cracking.

In the work reported in this paper, we have carefully matched the reactivity of the selected monomers to minimize segregation near the atomic level, using selected side groups that serve to prevent cross-linking between the growing oligomers, yet are easily removed by thermolysis. It was necessary to ensure that the silicon moieties were not prematurely volatized before condensing with the aluminum compounds.

Experimental Section

We approached the formation of mullite precursors with the intent of first achieving homogeneous polymerization between the silicon and aluminum monomers by matching the relative reactivity of the respective monomers, and second, preventing the premature loss of silicon by using less volatile silicon monomers. Systematic characterization of the growing polymer and of the final product were necessary to control the quality of the product. The monomers used in this study are listed in Table 1; schematics of some of the monomeric structures are shown in Figure 1. As we were seeking to prepare a poly(aluminosiloxane), the selected monomers had to satisfy two criteria: (i) both aluminum and silicon monomers had to have equivalent reactivities with respect to condensation while (ii) cross-linking between the growing polymers was reduced or avoided (e.g., condensation should preferentially result in linear copolymers containing both aluminum and silicon atoms in the molecular backbone), and (iii) organic side groups should be minimized to reduce the amount of material to be removed by subsequent processing.

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Table 2. Mullite Formation from Pure Precursors

	aluminum source	silicon source	phases present 800 °C	1000 °C	1350 °C	% mullite at process end
I	chelate	Al−O−Si	amorphous	γ-alumina and mullite	mullite	100
II	chelate	acetoxy	γ-alumina	γ-alumina	α-alumina and mullite	7.3
III	chelate	octamethylcyclotetrasiloxane	γ-alumina (trace)	γ-alumina	α-alumina and mullite	6.4
IV	chelate	diphenylsilanediol	amorphous	mullite	mullite	100
V	*sec*-butoxide	octamethylcyclotetrasiloxane	mullite (trace)	mullite	mullite	100
VI	*sec*-butoxide	acetoxy	mullite (trace)	mullite	mullite	100
VII	isopropoxide	tetramethylcyclotetrasiloxane		mullite	mullite	100

The sensitivity of the reactants to contaminants required that all synthesis glassware was scrupulously clean and that all reactions be run using standard Schlenk line techniques or in a nitrogen glovebox. The procedure involved soaking the glassware in KOH/ethanol solution for 12 h followed by soaking in 2 N HNO$_3$(aq) for 3 h. The glassware was removed from the cleaning solution, doubly rinsed with deionized water, and dried at 80 °C for 3 h. The dry glassware was transferred into a glovebox under a nitrogen atmosphere where the reagents were loaded into the distillation apparatus. The apparatus was removed to a fume hood and fitted (because of the high temperatures involved and the potential for highly exothermic reactions) with an explosion shield during reaction.

Prior to use, tetrahydrofuran (THF) was distilled over sodium/benzophenone ketyl under nitrogen and ethanol was distilled from magnesium ethoxide. Other reagents[32] were used as received. Sufficient amounts of the respective silicon and aluminum compounds were used in each mixture to set the Al/Si ratio in solution to 3.

For precursors **I**−**VI**, the monomers were placed in a flask and heated to 160 °C under dry nitrogen, at which temperature all were clear homogeneous liquids. Volatile components were then removed by heating the solutions to temperatures between 260 and 270 °C. The solubility of removed aliquots of the mixture in THF was monitored at every 10 °C increase in temperature to avoid converting the reaction mixture into an intractable and insoluble material. The use of a resin flask is particularly helpful for this reaction, easing removal of the product in the event intractable precursors are formed. THF was chosen as a good, nonhydroxylic solvent for the non-cross-linked materials but was a poor solvent for any crosslinked materials. Tractable intermediates were subsequently converted to oxide in standard air furnaces. Conversion heat treatments followed a simple two-step procedure: (i) initial heating to 800 °C at 1 °C/min followed by (ii) heating above 800 °C at 10 °C/min.

A high ceramic yield precursor, **VII**, was formed by hydrolyzing 2.14 g of tetramethylcyclotetrasiloxane (TMCTS) with 1 equiv of water in ethanol using one drop of methanesulfonic acid as a catalyst. The mixture was stirred until the heat of reaction had dissipated (30 min). Meanwhile, sufficient aluminum isopropoxide to give a 3:1 aluminum to silicon ratio was melted (150 °C) in a separate flask and then supercooled to 60 °C (this must be done carefully to avoid boiling the TMCTS mixture). The hydrolyzed TMCTS was added to the aluminum isopropoxide, and the resulting precipitate redissolved upon stirring the mixture overnight. The mixture was heated as before to drive off first the solvent and then the volatile byproducts of the condensation reaction.

The extent of polymerization during heating was monitored by collecting distillates at timed intervals for analysis by Fourier transform infrared spectrometry[33] (FTIR). Spectra of the liquid samples were obtained as neat thin films placed between KBr support plates. For solids, spectra were obtained by DRIFTS as dispersions in KBr powder. Separation and analysis of the distillate components was done using in-tandem gas chromatography/mass spectrometry[34] (GC/MS).

X-ray powder diffraction[35] (XRD) scans were run on dried and ground samples heat treated at 800, 1000, and 1350 °C to monitor the extent of crystallization and the phase composition of the precursors. Resident software diagnostics were used to estimate the percentages of the various phases present after the final heat treatment at 1350 °C. Differential thermal analysis[36] (DTA) studies were performed in air at heating rates of 1, 2, 5, and 10 °C/min, respectively, to confirm mullitization. Thermogravimetric analysis[37] (TGA) was used to characterize the weight loss of the precursor compounds during heating and to determine the amount of ceramic remaining after burnout.

The chemistry of the synthesized polymers was determined using FTIR and TGA. Small samples of the polymeric mixtures were removed from the reaction chamber during refluxing. It was observed that while the polymeric samples were slightly hygroscopic, the apparent rate of hydrolysis was slow enough to preclude special sampling techniques. Calcined samples were also characterized using FTIR and XRD.

Results and Discussion

The results of the phase analysis of precursors heated to high temperature are shown in Table 2. In the formation of the precursors, three stages of reaction were observed, delimited by the temperature of the reactant solution: (i) $T < 250$ °C, (ii) $250 < T < 300$ °C, and (iii) $T > 300$ °C. The first stage of reaction involved the evolution of alcohols and acetates, evidence that condensation was occurring between the monomers. In all aluminum-centered molecules, chelates were invariably found to be stable at lower temperatures, remaining bonded to the metal centers during condensation. At higher temperatures, traces of aluminum compounds appeared in the distillates in some cases, evidenced by the rapid formation of precipitates when the distillates were exposed to the atmosphere.

In mixtures of aluminum diisopropoxide acetoacetic ester chelate (APAE) with dimethyldiacetoxysilane (DMAS, **II**) and APAE with octamethyl cyclotetrasiloxane (OMTS, **III**), silicate esters containing random alkyl groups were detected in the distillate by GC/MS. Also present were ethers formed by the nonhydrolytic condensation of alkoxy groups, esters from the acetoxy ligands, and alcohols when hydroxyls (diphenylsilanediol and hydrolyzed TMCTS) were present. The production of silicate esters during low-temperature refluxing indicated that the reactivity of the chosen silicon monomer was too high, favoring reaction with alcohols or other byproducts of the reaction process present in the reaction vessel. The products of these unwanted reactions were volatile and evaporated from the reaction vessel, removing silicon from the reaction mixture, and ultimately lowering the reaction yields and preventing mullitization of the precursor. In mixtures **I** and **IV**−**VII**, no silicon was detected in the distillate during this reaction step.

(32) Aluminum compounds: Alfa Products, Danvers, MA. Silanes and siloxanes: Huls America, Bristol, PA. Tetraethoxysilane: Aldrich.
(33) Model 5DXB, Nicolet, Madison, WI.
(34) Model 5890A, Hewlett-Packard, Palo Alto, CA.
(35) APD 3720, Philips Electronic Instruments, Mount Vernon, NY.

(36) E. I. Du Pont de Nemours & Co., Wilmington, DE.
(37) Model TAS 7 thermal analysis system, Perkin-Elmer, Hartford, CT.

The onset of the second stage of the reaction process for mixtures **I**−**VII** was indicated by the increase in the temperature in the reaction vessel to temperatures above 250 °C. Above this temperature, chelate molecules and/or larger pendant groups (e.g., phenols) were detected in the distillate and silanol groups were detected in the reaction mixtures. The loss of the larger side groups from the reaction vessel was visible as the mixture became first colored and then darkened concomitant with a steady rise in the temperature of the reaction mixture. The deepening color accompanied a steady rise in the temperature of the reaction mixture as the side groups continued to be removed from the reaction vessel. TGA of the polymeric mixture revealed that most of the weight loss in the reaction vessel occurred between 250 and 300 °C, consistent with the loss of the protective side groups.

At temperatures above 300 °C a third stage of reaction was reached when the reaction mixture set and solidified due to extensive cross-linking (bridging) between the unprotected metal centers. A simple model of the ideal process can be described using the major chemical changes occurring in the reaction vessel: (i) In the first stage, condensation between the monomers releases the more volatile components from the monomer mixture. Meanwhile, the more tightly held chelates and phenyl groups protect the emerging oligomer from side reactions and prevent premature hydrolysis (and volatilization) of silicon compounds. (ii) The more protective side groups begin to come off at elevated temperatures, exposing the oligomer to cross-linking reactions. (iii) Finally, a critical amount of the remaining side groups is removed from solution, at which point the material sets.

Since one of our primary goals was the synthesis of *tractable* mullite precursors, tractibility in the reactant mixture was maintained by cooling the reaction vessel once the temperature was observed to rise above 250 °C. Subsequent studies (described in the following paragraphs) used only the tractable portion of the reaction mixture.

In Table 2 we show the evolving crystalline phase composition of the initially tractable precursors when calcined to 800, 1000, and 1350 °C, respectively. No further changes in composition were seen to occur above 1350 °C. Five of the mixtures in our study produced single-phase mullite by 1350 °C. As noted above, the two that did not convert completely to mullite (**II** and **III**) had suffered premature and substantial loss of silicon due to the volatility of silicon compounds formed during low-temperature reflux, evidenced by the low mullite content of the calcined solid. Where pure mullite was the final product (**I**, **IV**−**VII**), the lack of any detectable alumina indicated that the concentration of free silica was below 0.3% by weight (the detection limit of the spectrometer). Thus, the degree of mixing in the reaction vessel was very high and was retained during the condensation and cross-linking stages of the reaction.

We sought to prevent elemental segregation during the polymerization reactions in order to control the nucleation and growth of mullite at lower temperatures. Mixtures **I** and **IV**−**VII** all satisfied the first condition as the silicon content was maintained throughout the reaction. It was assumed that the stoichiometry of the mixture was fixed at the appropriate 3:1 Al/Si ratio since
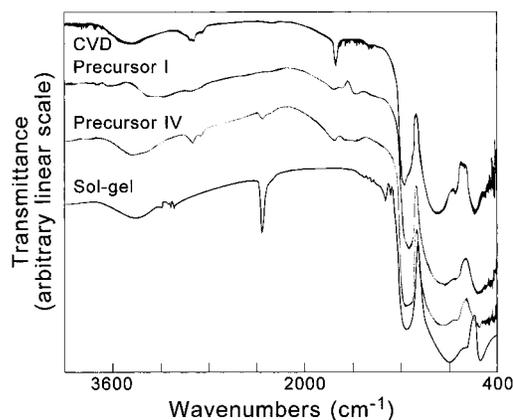

Figure 2. Chemical homogeneity in mullite prepared from polymeric precursors can be observed using FTIR. The above spectra show that mullite prepared from the precursors **I** and **IV** resemble the spectrum of mullite made by chemical vapor deposition. In contrast, a retained phase in mullite prepared from sol−gel is revealed by the presence of an infrared absorption band at ∼2340 cm⁻¹, probably due to the presence of constrained CO_2 in an amorphous phase.[38] (All samples but CVD mullite were heat treated to sufficiently high temperatures to ensure complete mullitization: 1000 °C for **IV**, and 1350 °C for **I** and sol−gel mullite.)

all eventually and completely converted to mullite. Evidence for satisfying the second condition was indirect: Mixture **I** obviously failed to maintain phase purity shown by the growth of γ-alumina in the matrix at 1000 °C. Further heat treatment completed the process to full mullite by 1350 °C, indicating that diffusion lengths remained fairly moderate after phase separation. Mixture **IV** remained amorphous up to 1000 °C, at which point mullitization was rapid and complete. Mixtures **V** and **VI** showed traces of mullite at 800 °C and were completely converted at 1000 °C. It was believed that the reactivity of the aluminum tri-*sec*-butoxide, used in both systems, closely matched that of the silicon compounds with respect to condensation. As a result, the precursors formed were chemically stable. However, both systems had low conversion yields, based on the starting materials.

These results also demonstrate that if sufficient care is given to the differences in reaction rates between the silicon and aluminum monomers, it is not necessary to use bulky ligands or chelating agents to ensure homogeneity. In the case of the high-ceramic-yield precursor, good homogeneity (evidenced by the mullitization temperature) can be obtained by the prehydrolysis of the silicon species, creating the more reactive Si−OH moieties. Again, maintaining a suitable reaction atmosphere obviates the need to protect aluminum with chelating agents as the aluminum monomer will be reasonably stable in the absence of water.

In earlier work we have described the presence of an infrared absorbance at ∼2340 cm⁻¹ in mullite caused by the retention of a silicon-rich phase after complete conversion of the matrix.[19] This absorption band provides a method for characterizing the extent of chemical homogeneity in the precursor, being absent in truly chemically homogeneous systems (e.g., in mullite made using chemical vapor deposition). It is likely that this absorption arises from the constrained vibrations of CO_2 trapped within an amorphous phase present in the mullite matrix.[38] The CO_2 remains from the thermolytic
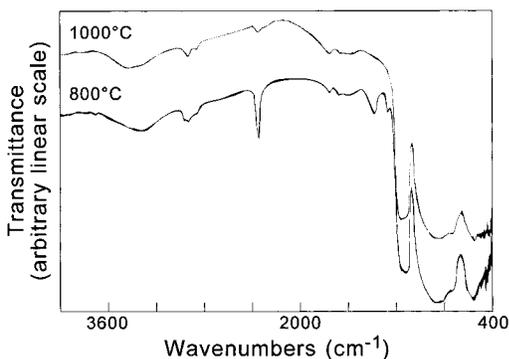
Figure 3. Transient phase separation in a mullite precursor can be observed using the absorption band at ~2340 cm^{-1}. At 800 °C, the precursor mixture **IV** is amorphous by X-ray diffraction (Table 2), but IR analysis shows a mullite stoichiometry already exists in the matrix. Phase separation is also apparent in the presence of the 2340 cm^{-1} band and silica absorbances. When heated to 1000 °C, mixture **IV** completely transforms to mullite with little remaining phase segregation.

decomposition of the organic moieties in the original material. Better (e.g., smaller scale) mixing of the precursor chemicals reduces the amount of amorphous phase and thereby decreases the retention of CO_2.

In Figure 2 we show representative spectra of mullite formed by CVD and from two of our polymeric precursors. In the case of both CVD mullite and mullite formed from the homogeneous precursor mixtures **I** and **IV**, the 2340 cm^{-1} band either does not appear or is greatly attenuated in the final product. For contrast, a high purity mullite formed from a sol−gel precursor shows that, at this degree of homogeneity, a second, amorphous phase is retained after mullitization appears complete.[19] Phase separation during the mullitization process can be observed using this same absorption band. In Figure 3, we can see that at 800 °C, a mullite stoichiometry is present in precursor **IV** and that phase separation exists to some extent (evidenced by silica absorption bands as well as the band at 2340 cm^{-1}). After mullitization is completed at 1000 °C, only a trace of the second phase remains, indicating the high degree of homogeneity achieved from the original precursor.

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Summary and Conclusions

Tractable aluminosiloxane precursors have been made that convert to mullite at ~1000 °C. Homogeneity was controlled by the use of appropriate monomers, shown in Table 2. Crystalline mullite nucleation was not required for low temperature conversion; in our observations, better yields were achieved using materials that remained amorphous up to ~1000 °C (**I**, **IV**). Although low-temperature (<1000 °C) phase separation was observed by XRD in one of the amorphous systems (**I**), the diffusion lengths remained short and full mullitization was achieved by 1350 °C. In the second amorphous system (**IV**), mullitization was completed at 1000 °C, and XRD characterization indicated that the matrix was single phase throughout mullitization. However, infrared analysis of this system indicated that while the material had mullite stoichiometry at 800 °C, the presence of an absorption band near 2340 cm^{-1} was evidence that some degree of phase separation existed in this compound at 800 °C. In this case, the diffusional lengths were apparently very small as the material fully converted to mullite by 1000 °C. In mixture **VII**, a high ceramic yield, tractable polymer was obtained without the need for the higher reaction temperatures by choosing starting materials with low organic content and utilizing a prehydrolysis step to match the reactivity of the silicon and aluminum monomers.

Precursors with high ceramic conversion yields are important particularly for the impregnation of powder compacts to make monolithic ceramics and/or ceramic/ceramic composites. Because of shrinkage due to solvent loss and organic burnout, a single impregnation step is likely to fill less than 10% of the void space in a compact. More efficient filling of the void space reduces the number of necessary impregnations. Reducing the void volume within a porous ceramic compact speeds the densification of the monolith while preventing deleterious shrinkage, thus these new materials provide effective processing aids for the production of films and monoliths from powder compacts.