Journal of the European Ceramic Society 18 (1998) 1765–1769
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PII: S0955-2219(98)00087-9 0955-2219/98/$—see front matter

Formation of Mullite Phase in Diphasic Gels Consisting of TEOS and Boehmite With and Without Dehydroxylation

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(Received 27 October 1997; accepted 4 March 1998)

Abstract

Mullite ($3Al_2O_3\ 2SiO_2$) samples have been prepared from mixture of TEOS and boehmite, with and without dehydroxylation at 400°C. The precursor samples during the process of phase formation were characterized with respect to TGA, DTA, TMA, and X-ray diffraction at various temperatures. The result shows that by using a partially dehydroxylated boehmite, an enhanced transitional alumina phase is found at a lower temperature (~1000°C) along with traces of α-Al_2O_3. With an increase in soaking time, the intensity of α-alumina is often found to increase. The formation of mullite takes place at 1225°C and the α-Al_2O_3 formed at a lower temperature remains unaffected even at 1500°C. On the other hand, in the samples prepared from boehmite and TEOS, the transitional alumina phase is observed only at 1225°C and it transforms to phase pure orthorhombic mullite at 1250°C. Thus while the partially dehydroxylated boehmite appears to be more reactive to transform to transitional alumina phase at lower temperature, the mullite formation temperature does not occur below 1225°C. The results of investigation are presented and discussed. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

Mullite is the stable compound with high crystallinity in the SiO_2–Al_2O_3 system and has important thermomechanical properties like low thermal expansion, low thermal conductivity, excellent creep resistance, good chemical stability and oxidation resistance which have made it a strong candidate material for advanced structural and functional ceramics in recent years.[1] Mullite has also received much attention as matrix for ceramic composites, in electronic packaging and for optical applications.[1]

Mullite is generally prepared by thermal reactions of alumina and silica in stoichiometric proportions above 1450°C. The reaction rate and phase development sequences depend up on the specific processing route.[2–17] Reaction sintering of quartz and submicron α-Al_2O_3 was reported and the reactions have been followed by transmission electron microscopy (TEM). The reaction sequence starts with formation of a transient melt layer on the surface of the quartz grain. Mullite formation occurs mainly at the α-Al_2O_3 grain junctions and less frequently, inside the bulk of the liquid.[18] Crystallization of coprecipitated mullite precursor during heat treatment shows that during calcination below 1100°C, γ-Al_2O_3 and perhaps cristobalite crystallites are formed and at 1200°C, mullite being formed by the reaction between γ-Al_2O_3 or θ-Al_2O_3 with silica through a diffusion controlled process.[16] Sol–gel methods have been employed widely in the synthesis of mullite either through boehmite (AlOOH) and TEOS or through $Al(NO_3)_3$ and TEOS mixtures.[14] The reaction sequence appears to be rather precursor dependent. Ph. Colomban could observe by IR and Raman studies that the use of alkoxide with long chains favours heterogenities. However the mullite gels seem to have the same structure as the alumina gel and the presence of silicon alkoxide regularises the aluminium butoxide hydrolysis and favours the homogeniety.[19] Different pore size distributions are observed for aluminosilicates prepared by hydrolysis of an Si–O–Al ester and the sintering is found to be directly related to the densification of the polymeric network.[20] Earlier reports indicate that precursors containing boehmite–TEOS mixtures lead to form mullite by first forming Al–Si spinel or γ-Al_2O_3 which gets converted to θ-Al_2O_3 which in turn reacts with amorphous silica to form mullite depending upon Al_2O_3/SiO_2 ratio.[21] On the other

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*To whom correspondence should be addressed. Fax: 0091 0471 491712; e-mail: warrier@csrrltrd.ren.nic.in hand, xerogels consists of bayerite and TEOS, the η-Al_2O_3 formed initially transforms to θ-Al_2O_3 and later reacts with amorphous silica to form mullite.[21] Generally in some diphasic gels, the mullite is formed by the reaction between amorphous silica and transitional alumina, and the mullitization temperature is in the range 1200–1350°C depending on the source and nature of alumina and silica.[2–17] Many evidences suggest that in diphasic gels, rate determining step for the growth of mullite is the dissolution of alumina in the silicious phase.[22–24] Wang and Sacks studied the formation of mullite using microcomposite powders which consists of α-alumina cores and amorphous silica coatings and found that α-alumina-amorphous silica reaction to form mullite is endothermic at around 1490°C.[25] Gerardin *et al.* showed the reaction between spinel and amorphous silica is more endothermic than corresponding reaction with α-Al_2O_3.[11] On the other hand, it is also known that the formation of mullite at high temperature between bulk samples of α-Al_2O_3 and silica occurs through nucleation at the interface between the two phases and the growth is controlled by interdiffusion of aluminium and silicon ions, through the mullite layer.

Sol–gel alumina precursors have been found to respond favourably to enhance the high temperature phase transformation in presence of nucleating centres or seeds[26] and mullite system has also been known to respond in a similar way. Addition of 2wt% γ-Al_2O_3 seed particles to the boehmite–TEOS system is reported to reduce the transformation temperature of mullite, by possibly making available sufficient δ, θ-alumina phase at low temperatures for reactions.[27] In such cases, finely dispersed γ-alumina rich phase in the precursor should enhance the reaction with silica compared to other precursor systems. Such study appears novel and has not been reported earlier. The present work concentrates on the study of mullite formation characteristics of precursor containing partially dehydroxylated boehmite + TEOS and boehmite + TEOS mixtures. The results of the investigation are reported.

2 Experimental Procedure

The materials used in the experiments were boehmite (Condea Chemicals, Germany) and tetraethylorthosilicate (TEOS) (Alfa Chemicals, USA). Mullite precursor samples were prepared through different routes. Diphasic mullite precursor gel was prepared from boehmite sol and TEOS. Boehmite sol was first prepared by dispersing boehmite (Condea Chemicals, Germany) in doubly distilled water followed by peptizing to a sol using 10% dilute nitric acid at pH 3. The concentration of the sol was $1{\cdot}03\times10^{-2}$ g Al_2O_3 ml^{-1}. In a typical experiment, 9·8 ml TEOS stabilized in 50 ml ethanol was added dropwise to 703·9 ml of boehmite sol of pH 3 during constant stirring. After mixing TEOS and boehmite sol, the pH of the medium was raised to 8 by addition of dilute ammonia solution. The mixture was ball milled for 6 h and dried under conditions of 45°C and 65% relative humidity.

In another experiment, 9·66 g boehmite was calcined at 400°C for a period of 5 h to get γ-alumina rich dehydroxylated boehmite which was further dispersed in 500 ml distilled water, adjusting the pH to 4 by adding 10% dilute nitric acid followed by ball milling for 5 h using alumina grinding medium. 9·8 ml TEOS stabilized in 50 ml ethanol was added dropwise to the alumina dispersion under strong stirring. The pH of the solution was raised to 8 by adding dilute ammonia solution and the slurry was dried in humidity oven as before.

The thermal analysis of the samples were carried out in Shimadzu DTA 50H and TGA 50H thermal analyser respectively in nitrogen atmosphere at a heating rate of 10°C min^{-1}. The thermomechanical analysis was done in Shimadzu TMA 50H on cylindrical samples of size 7 mm diameter and 12 mm length at a heating rate of 10°C m^{-1}. XRD patterns of the samples were taken using X-ray diffractometer (Philips–1710, Netherlands) in the 2θ range 20–60°. The mullite precursor gels calcined at 600°C were made into pellets of 10 mm. diameter and 2 mm thickness by uniaxial pressing and sintered at 1500°C and the densities were measured using Archimedes' principle. The fractograph of the sintered samples were taken using a Hitachi (S-2400), Japan scanning electron microscope.

3 Results and Discussion

The mullite precursor gel prepared from boehmite sol shows a three step decomposition pattern (Fig. 1). The first step corresponds to the removal of moisture, second step corresponds to the volatiles and then the third step to the dehydroxylation of solvated water in the precursor. The total weight loss is found to be ~29%. The mullite prepared from boehmite calcined at 400°C–TEOS mixture had a total weight loss of only 17%. This lower weight loss is due to the early elimination of free water of boehmite. The DTA patterns of mullite precursor gel prepared from TEOS–boehmite mixture and that from boehmite calcined at 400°C, presented in Fig. 2 are nearly identical. The broad exotherm in the range 1200–1300°C indicates the formation of mullite. In diphasic gels the DTA

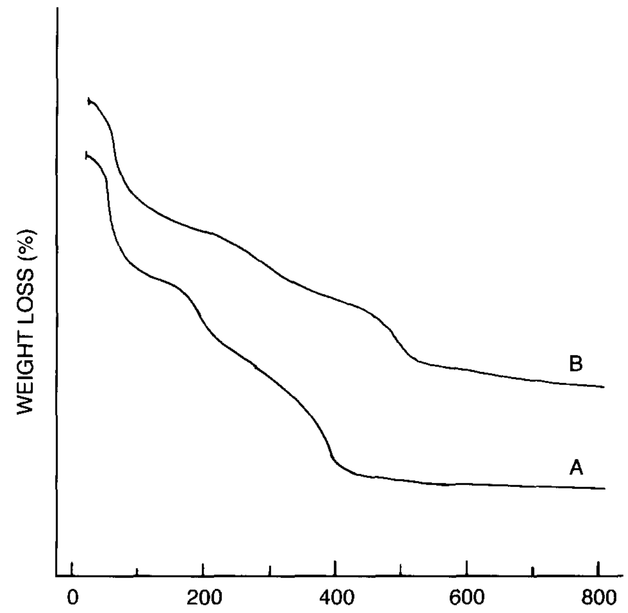

Fig. 1. TGA curves of mullite precursor from (A) boehmite + TEOS and (B) dehydroxylated boehmite + TEOS.

usually indicates formation of mullite as exotherm between 1250–1300°C.[28] On the other hand, mullitization reaction in monophasic gels is widely reported at ~980°C.[28] The derivative thermomechanical analysis curves of samples are presented in Fig. 3. The boehmite–TEOS mixture indicates shrinkage starting below 1000°C gradually extending to temperature above 1300°C, while the one containing a mixture of calcined boehmite and TEOS has an initial shrinkage at about 1000°C followed by another shrinkage at about 1250°C, indicating that the reaction follows two steps in the latter. The former could be the formation of transitional alumina phase along with silica, while the latter could be the formation of mullite phase and subsequent densification.

In order to study the phase formation characteristics, the samples were calcined at various temperatures and were analysed using XRD data. The XRD pattern of mullite precursor sample prepared from boehmite calcined at 400°C and TEOS, heated to 1000°C for 3 h [Fig. 4(A)] is nearly amorphous but with minor indication of transitional and α-Al_2O_3 phases. As the soaking time increases to 6 h, the intensity of α-Al_2O_3 peaks is slightly enhanced [Fig. 4(B)]. The XRD pattern of the sample heated to 1200°C shows more α-Al_2O_3 along with transitional alumina [Fig. 4(C)], and as the soaking time increases to 6 h, the intensity of α-Al_2O_3 peaks is enhanced, but no mullite peaks are observed [Fig. 4(D)]. At 1225°C for a period of 3 h, mullite prepared from calcined boehmite shows the presence of mullite peaks with α-Al_2O_3 [Fig. 5(C)]. As the soaking time increases to 6 h, the intensity of α-Al_2O_3 phase is enhanced [Fig. 5(D)], but no enhancement is observed for mullite peaks. On the other hand, the gel sample prepared from boehmite sol and TEOS, shows only transitional alumina

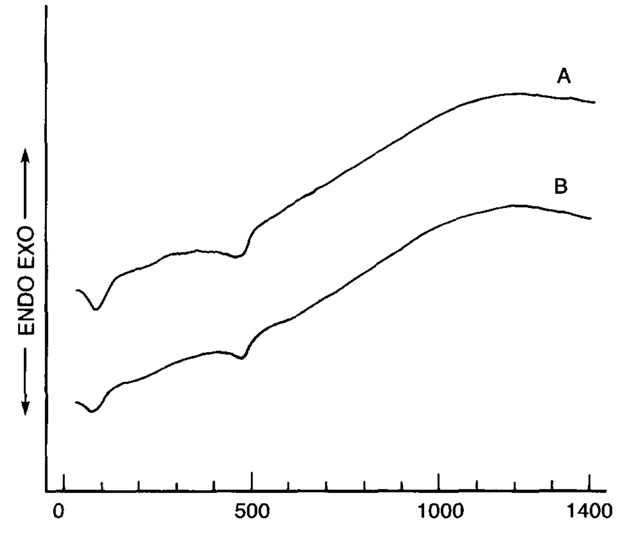

Fig. 2. DTA curves of mullite precursor from (A) boehmite + TEOS and (B) dehydroxylated boehmite + TEOS.

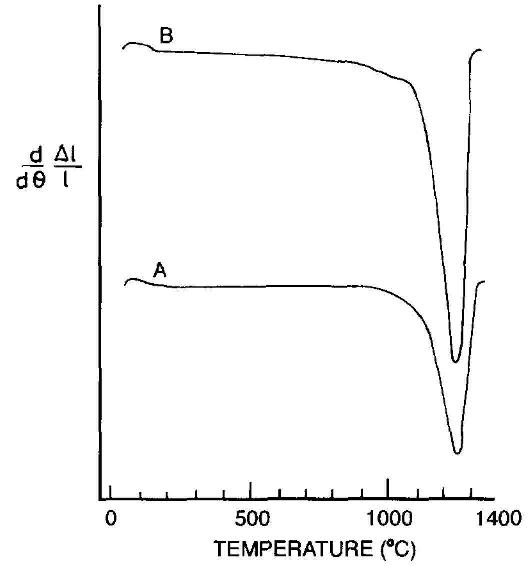

Fig. 3. Derivative TMA curves of mullite precursor from (A) boehmite + TEOS and (B) dehydroxylated boehmite + TEOS.

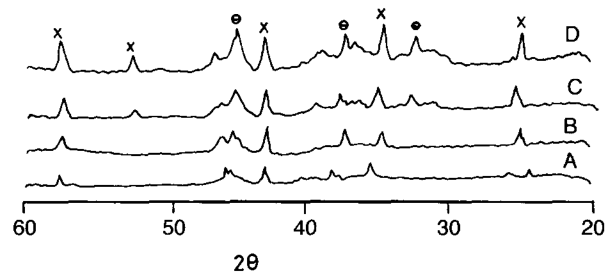

Fig. 4. XRD patterns of mullite precursor prepared from dehydroxylated boehmite. (A) 1000°C 3 h^{-1}; (B) 1000°C 6 h^{-1}; (C) 1200°C 6 h^{-1}; (D) 1200°C 3 h^{-1}. (o, Mullite; x, α-alumina; θ, θ-alumina).

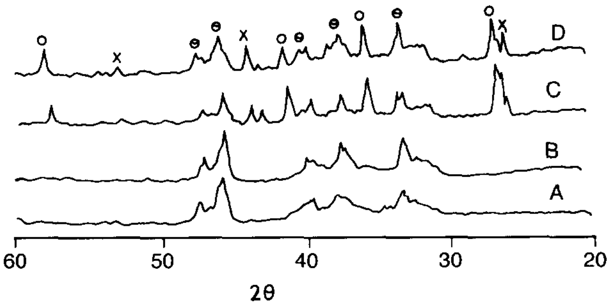

Fig. 5. XRD patterns of mullite precursor prepared from (A) boehmite + TEOS 1200°C $3\,h^{-1}$; (B) boehmite + TEOS, 1225°C $6\,h^{-1}$; (C) dehydroxylated boehmite + TEOS, 1225°C $3\,h^{-1}$; (D) dehydroxylated boehmite + TEOS, 1225°C $6\,h^{-1}$. (o, Mullite; x, α-alumina; θ, θ-alumina).

phase at 1200°C [Fig. 5(A)]. This phase is retained when calcined at 1225°C even for 6 h [Fig. 5(B)], which further converts to phase pure orthorhombic mullite at 1250°C/3 h. No other phase like α-alumina or cristobalite is present [Fig. 6(A)]. However, traces of α-Al_2O_3 and transitional alumina are still present in the precursor prepared from dehydroxylated boehmite in the samples and remain unreacted with silica even at 1300°C [Fig. 6(B)]. On the contrary, since the mullite formation is achieved earlier to densification, this sample has a lower density of ~90%, much less than boehmite–TEOS mixture (98%), on sintering at 1500°C. At 400°C, boehmite is partially dehydroxylated and the γ-Al_2O_3 thus formed enhances the transformation of boehmite to transitional alumina as in the case of γ-Al_2O_3 seeded boehmite[26] and since transitional alumina silica reaction occurs more favourably, mullite phase is formed at a lower temperature. Meanwhile, the transitional alumina phase formed at lower temperature gets transformed to α-alumina preferentialy leaving less of transitional alumina for reaction with TEOS. Since α-alumina–silica reactions are well known to be sluggish,[25] α-alumina is retained even on prolonged heating. On the other hand, in the case of boehmite–TEOS, the transitional alumina is available around 1200°C, and hence complete conversion to mullite takes place at 1250°C with out preferential conversion to α-alumina. This is also clear from the fractographs presented in Fig. 7. The boehmite–TEOS mixture derived sintered mullite has no second phase is nearly sintered to full density, although has been associated with large grain growth [Fig. 7(A)]. On the other hand, the calcined boehmite–TEOS precursor results in a less dense microstructure indicating also a distribution of unreacted second phase containing α-alumina [Fig. 7(B)] The reason for the lower sintered densities is also the presence of α-alumina phase remaining unreacted with TEOS. Thus the results show that prolonged soaking at lower tem-

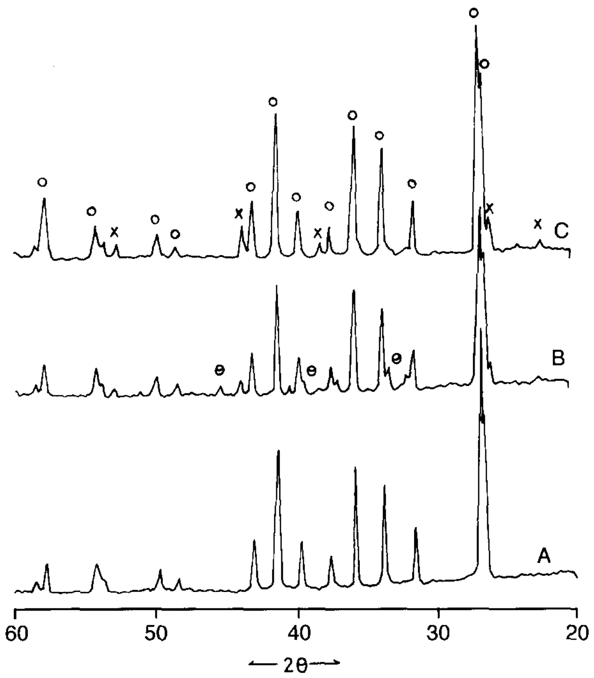

Fig. 6. XRD patterns of mullite precursor prepared from (A) boehmite + TEOS 1250°C $3\,h^{-1}$; (B) dehydroxylated boehmite + TEOS, 1300°C $3\,h^{-1}$; (C) dehydroxylated boehmite + TEOS, 1500°C $3\,h^{-1}$. (o, Mullite; x, α-alumina; θ, θ-alumina).

(a)

(b)

Fig. 7. Fractographs of mullite samples sintered at 1500°C $2\,h^{-1}$ prepared from (A) boehmite sol + TEOS; (B) dehydroxylated boehmite + TEOS.

perature results in the formation of α-Al_2O_3 phase while soaking at higher temperature is better for mullite formation, in the case of diphasic precursors.

4 Conclusion

The present investigation has indicated the possibility of obtaining earlier mullite formation in diphasic precursor mullite gels containing calcined boehmite (γ-alumina rich phase) and TEOS where the transitional alumina phase becomes available at as low as 1000°C. However, traces of α-Al_2O_3 which remain unreacted are present even after heating to higher temperatures. On the other hand, mullite precursor from boehmite–TEOS mixture becomes completely transformed to orthorhombic mullite at 1250°C and sinters to density 10% higher than the former. The present study reveals that even though transitional alumina is made available even at 1000°C, the reaction with TEOS to form mullite starts only at 1200°C or above, and prolonged heating of the transitional alumina–TEOS mixture below 1250°C results only in enhanced α-alumina phase. Such precursor further leaves second phase containing α-alumina having lower densities even in sintered mullite. On the contrary, enhanced mullite formation is possible only above 1225°C even in presence of adequate transitional alumina phase at still lower temperatures in diphasic precursor which also sinters to higher densities.

Acknowledgement

One of the authors, G.M.A., acknowledges Council of Scientific and Industrial Research (CSIR), India, for a Senior Research Fellowship.

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