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Synthesis and Phase Transformations of Mullites Obtained from SiO_2–Al_2O_3 Gels

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Abstract

Synthesis and structural characterization of mullite phases obtained from three nominal compositions in the SiO_2*–*Al_2O_3 *system is reported and comparisons between them are established. Monosized gels with Al/Si atomic ratios of 2 : 3, 3 : 1 and 9 : 1 were obtained and thermally treated at temperatures between 700 and 1500°C. The thermal evolution of amorphous gels was followed by thermal analysis, X-ray diffraction and infra-red spectroscopy. The microstructural changes were studied by scanning electron microscopy and transmission electron microscopy. The formation of* Al_2O_3*-rich mullite started around 1000°C for all samples and was fully developed at 1400°C. The chemical composition of mullites changed as a function of calcining temperature. An anomalous low value of the lattice parameter* a *was obtained for the sample with Al/Si atomic ratio of 9 : 1 compared with the 3 : 1 sample at 1400°C, which may be due to the slow reaction rate of* Al_2O_3 *with* SiO_2*-rich glassy phase during mullite formation.*

1 Introduction

Mullite is the only stable phase in the SiO_2–Al_2O_3 binary system. The properties of this phase are of great technological importance because of its high mechanical strength at high temperatures and its optical characteristics,[1] so that mullite has long been the subject of intense research. However, research at a fundamental level on thermodynamics, kinetics and crystal structure is needed to clarify some aspects that are not completely understood yet.

An early way for synthesizing mullite, reported some years ago, was the thermal decomposition of kaolinite: in this process, by maintaining an almost topotactic relationship between phases and with the release of SiO_2, mullite is obtained as end product. The so-called 'sol–gel' process, widely used for the preparation of materials during the past few years, has recently been applied to the preparation of aluminosilicates. Two methods have been used to achieve the synthesis of pure mullite powders, these ways differing in the degree of homogeneity of the precursor. Thus, when the scale of chemical homogeneity is at the atomic level, mullite formation is observed at ~980°C through an exothermic reaction. In contrast, when the scale of chemical homogeneity is in the nanometer range (the so-called diphasic precursors), the formation of mullite is delayed to temperatures higher than 1200°C. Both crystallization processes are evidenced by exothermic effects in differential analysis curves. The mullite formation kinetics in both cases has been observed to follow a nucleation and growth process but whereas in the single-phase precursor the process of mullitization is consistent with a nucleation rate-controlled mechanism, in the case of diphasic precursors it has been found that the growth rate of the mullite grains is controlled by dissolution of the alumina particles into the amorphous silica-rich phase.[2,3] Another way of synthesizing mullite is from the so-called hybrid gels, defined as gels from mixtures of polymeric and colloidal derived sols. By low temperature treatment, *in situ* crystallization of the polymeric gel is effected, thus obtaining mullite seed crystals in an untransformed matrix; then mullite nucleates homoepitactically from the viscous densified colloidal gel. Further research may be interesting to achieve new processing methods at lower temperatures mainly to obtain precursors in which aluminium and silicon are at a real atomic level of mixing.

The structure of mullite may be thought of as being derived from the disordered sillimanite $SiO_2 \cdot Al_2O_3$, by the exchange of Al^{3+} for Si^{4+} and the removal of oxygen anions.[4] The stoichiometric phase may be written as $[Al_2]^{VI}(Si_{2-2x}Al_{2+2x})^{IV}O_{10-x}$

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and corresponds to a crystalline phase with variable composition, i.e. a solid solution. In order to accommodate this compositional variation, mullite develops an incommensurate structure whose periodicity varies continuously with composition.

The metastability of the pseudo-tetragonal crystalline modification and the tetragonal ↔ orthorhombic transition have been dealt with previously. Cameron[5] showed the possibility of obtaining a tetragonal phase for x about 0·65, corresponding to 79 mol% Al_2O_3. However, mullites containing more than 77·3 mol% Al_2O_3 have not been reported, this being the main reason why Cameron's suggestion on the occurrence of mullite with tetragonal symmetry has not been confirmed or denied. Schneider *et al.*[6] have recently reported a metastable orthorhombic mullite phase with $a > b$ obtained from a starting mixture of aluminium sec-butylate and silicon chloride with an Al/Si ratio of 8 : 1 (i.e. $x = 0{\cdot}67$, corresponding to 80·2 mol% Al_2O_3). That metastable mullite has a composition richer than $x = 0{\cdot}65$ in Cameron's diagram, at which point the curves of a and b cell parameters cross.

Many studies on mullite formation from gel precursors with different Al/Si ratios have been reported. The reactions leading to the formation of mullite can vary considerably depending on the method of preparation of gels, i.e. single phase or diphasic gels. Several reports have examined the effect of Al/Si ratio on the formation temperature and the microstructure of mullite from diphasic gels.[7] However, when alumina and silica are mixed on a molecular level as in the case of single-phase gels, little information exists concerning the effect of Al/Si ratio on mullitization temperature and microstructure[8] for compositions placed far away from the stable or metastable mullite solid-solution boundaries in the SiO_2–Al_2O_3 binary system. Some experimental factors can affect directly the precursor gel structure which determines the further thermal evolution. One of the key points is to avoid the occurrence of alumina segregation while hydrolysis and condensation reactions take place. One of the possible ways to overcome this difficulty is, as previously reported for other systems,[9] to use prehydrolysed tetraethylorthosilicate (TEOS) solution as silicon source.

The aim of this work was the preparation and characterization of mullite powders in the binary system starting from mixtures of prehydrolysed TEOS and aluminium alkoxides. Three different compositions, corresponding to $Al_2O_3 : SiO_2$ molar ratios of 1 : 3, 3 : 2 ($x = 0{\cdot}25$) and 9 : 2 ($x = 0{\cdot}70$) — the former and latter placed in both sides of the solid solution limit composition for mullite, have been prepared as single-phase gels. The structural evolution with thermal treatment for specimens of different Al/Si ratios and the microstructural features of starting gels and final products were also examined.

2 Experimental Procedure

2.1 Preparation of gel samples

Gels with compositions (in mol%) 25 Al_2O_3 : 75 SiO_2 (hereafter denoted as sample A, with composition in wt% 36·1 Al_2O_3 and 63·9 SiO_2) and 60 Al_2O_3 : 40 SiO_2 (hereafter denoted as sample B, with composition in wt% 71·8 Al_2O_3 and 28·2 SiO_2) were prepared using as starting chemicals tetraethylorthosilicate (TEOS, $Si(OC_2H_5)_4$) and aluminium ethoxide ($Al(OC_2H_5)_3$), both from Merck & Co. (Darmstadt, Germany) by the following procedure.

The $Al(OC_2H_5)_3$ was dissolved in ethanol (EtOH) by refluxing and added to a prehydrolysed TEOS solution. The TEOS : H_2O molar ratio used was 1 : 2 and prehydrolysis performed at 40°C for 20 h. The resultant mixture was refluxed at 70°C for 5 days. After several days sample B, with the larger amount of aluminium alkoxide and consequently requiring a higher molar ratio of TEOS/EtOH (1/30) than sample A (1/20), gave rise to a transparent gel. On the other hand, sample A gelled after mixing both starting solutions and gave a gel that was opaque.

A gel with composition (in mol%) 81·8 Al_2O_3 : 18·2 SiO_2 (hereafter denoted as sample C, with composition in wt% 88·4 Al_2O_3 and 11·6 SiO_2) was prepared using aluminium tri-sec-butylate ($C_{12}H_{27}AlO_3$) from Merck as raw material and isopropanol as solvent. These changes in reagents facilitate the dissolution of a great amount of aluminium raw material. The procedure followed for preparing gel C was the same as for gels A and B, using a molar ratio TEOS/Si-PrOH = 1/30. After several days a transparent gel was obtained.

To check possible differences in structure and phase transformation of dried and heated gels when aluminium tri-sec-butylate and isopropanol were used instead of aluminium ethoxide and ethanol in the preparation of gels, composition B was prepared with both aluminium alkoxides and solvents.

All gels were first slowly dried by covering the beaker containing the gel with a holed plastic film and allowing the solvent to evaporate for several weeks; they were then dried in oven at 120°C. Dried gels A and B showed a yellow colouration while dried gel C was colourless.

Precursor glass gel was obtained by preheating the dried samples at 750°C for 3 h, products derived from this process were either grey (sample B) or white (samples A and C). Glass powder was calcined at temperatures in the range 900 to 1400°C for 3 to 15 h, or at 1500°C for 30 min.

2.2 Characterization of samples

The chemical and structural evolution of dried gels and crystalline specimens was examined using several techniques.

Infra-red (IR) absorption spectra were obtained in the range 2000–400 cm^{-1} using the KBr pellet method on a Perkin–Elmer model 882 spectrometer (Beaconsfield, UK).

Differential thermal analysis (DTA) [Perkin–Elmer model 1700 instrument (Norwalk, CT)] and thermogravimetric analysis [Perkin–Elmer model 7 instrument (Norwalk, CT)] were carried out in air with α-Al_2O_3 liners, using a heating rate of 10°C min^{-1}. Finely powdered alumina was used as reference substance.

X-ray diffraction (XRD) analysis (model D-500 diffractometer, Siemens, Karlsruhe, Germany) was performed using graphite-monochromated Cu $K\alpha$ radiation. The diffractometer had two 1° divergence slits, a 1° scatter slit, and a 0·05° receiving slit. Eleven overlap-free reflections between 20° and 70° (2θ) were measured with a scanning speed of 0·12° 2θ min^{-1} using CaF_2 as internal standard. Determination of the lattice constants of mullite was made using LSQC and POWCAL programs.

The microstructure of the as-prepared and thermally treated samples was determined by scanning electron microscopy (SEM) and field-emission SEM working at 20–30 kV and 5–10 kV, respectively (models S-2500 and S-4100, Hitachi Ltd, Tokyo, Japan). To check the quality of the observation, some of the samples were etched with dilute HF solution for 10 s, and subsequently washed with H_2O. All specimens were coated with gold in an ion-beam coater. The morphology of dried gels and mullite particles was also examined using transmission electron microscopy (TEM) (model H-800, Hitachi Ltd, Tokyo, Japan) at an accelerating voltage of 200 kV. Samples were prepared by dispersing as-produced and calcined powders in absolute ethanol and setting dropwise on copper grids that had previously been coated with a holey thin carbon film.

3 Results and Discussion

3.1 Structural development of gel samples

Since two kinds of aluminium precursor were used for gel preparation, we think it is worthwhile to comment that the gel structure and experimental results for thermal-treated specimens B prepared from both types of aluminium source and solvent are very similar. Therefore, it can be assumed that experimental results of all three compositions prepared in this work are comparable with each other.

IR spectra of dried gels and crystalline samples are depicted in Figs 1, 2 and 3. In comparison

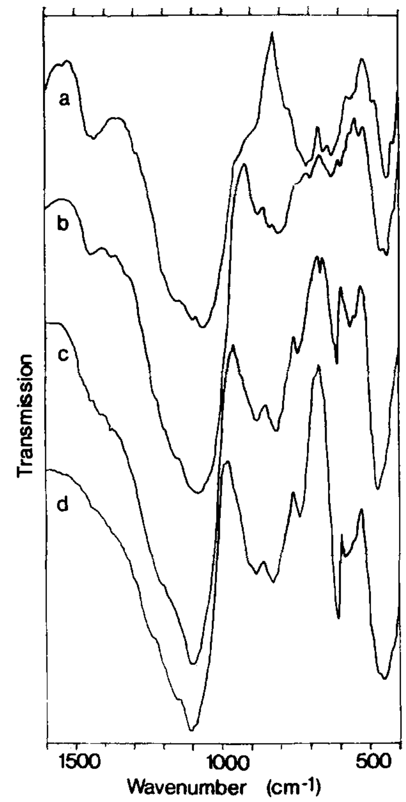


Fig. 1. IR absorption spectra of sample A gels after several heat treatments: (a) dried gel; (b) 750°C/3 h; (c) 1000°C/3 h; (d) 1300°C/3 h.

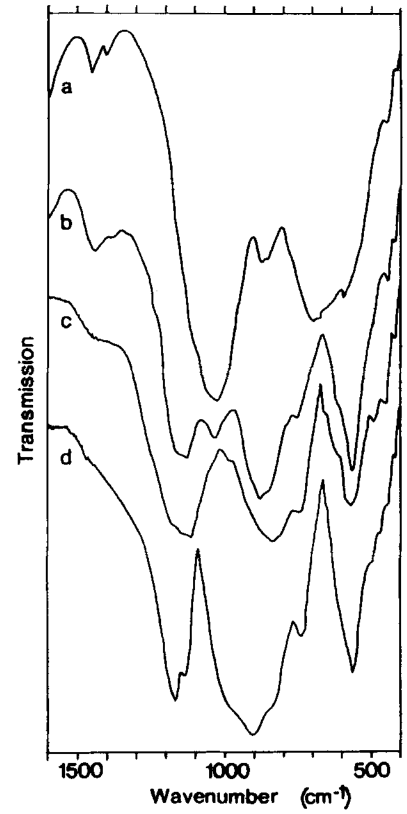


Fig. 2. IR absorption spectra of sample B gels after several heat treatments: (a) dried gel; (b) 750°C/3 h; (c) 1000°C/3 h; (d) 1300°C/3 h.

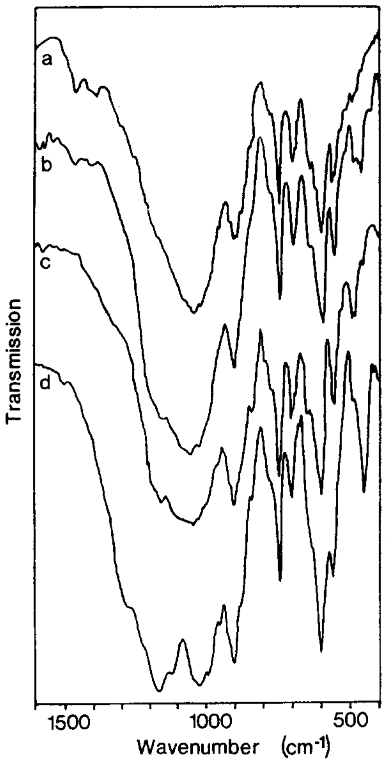


Fig. 3. IR absorption spectra of sample C gels after several heat treatments: (a) dried gel; (b) 750°C/3 h; (c) 1000°C/3 h; (d) 1300°C/3 h.

with IR spectra observed in previously reported binary systems,[10,12] the characteristic vibration modes associated with Si–O bonds were not so clearly distinguished in samples B and C. On the other hand, peaks in the 500 to 800 cm^{-1} region were clearly observed in both samples (although more intense in sample C), and can be attributed to Al–O bonds both in tetrahedral and octahedral coordination. For both samples B and C a band centred at 875 cm^{-1} was observed over the full range of temperature, increasing its intensity with higher temperatures. This band could be associated with Si–OH and/or Al–OH at low temperature; however it also may be attributed to Si–O–Al bond vibrations.[13,14] The peak at 1020 cm^{-1} was attributed to Si–O bond stretching vibration modes. Other authors associate this band with Si–O–Al bond vibrations because the absorption band of Si–O bonds at 1100 cm^{-1} for amorphous silica is shifted to lower energies by introducing Si–O–Al bonds.[10,12] This band shifted to higher energies with increasing temperature: thus, at 1300°C the band from 1020 cm^{-1} was centred at 1165 cm^{-1} with a shoulder at 1130 cm^{-1} associated with SiO_4 and AlO_4 tetrahedra vibration modes, respectively. It should be noted that in samples treated at temperatures higher than 1300°C all characteristic bands of mullite were observed (1175, 1120, 905, 845, 750 and 460 cm^{-1}).[11]

In general, there was an apparent difference between the IR spectra of sample A and those of samples B and C. As can be seen, bands around 1200, 1100, 750 and 460 cm^{-1} attributed to Si–O bonds were detected in the former dried gels. In samples of gel A shifting to higher wavenumber with the formation of mullite at 1000°C was very small compared with the deviations detected in sample B, richer in Al_2O_3. An increase of band intensity associated with Si–O–Si bonds was observed, mainly for the peaks around 440 and 1030 cm^{-1}, compared with both bands in sample B. This fact could be due to an increasing amount of SiO_2 which does not form mullite.

Some authors[12,15] have reported the chemical composition of mullite as a function of the absorbance bands at 1130 and 1165 cm^{-1}. When the chemical composition of mullite is rich in Al_2O_3, the 1130 cm^{-1} peak is stronger than the 1170 cm^{-1} peak in intensity. In samples B and C at 1300°C, the 1165 cm^{-1} peak was stronger than that at 1130 cm^{-1}. It was not possible to draw comparisons between peaks in sample A because bands associated with the excess silica overlapped with the corresponding bands of mullite. It is noteworthy, however, that the band at 1130 cm^{-1} in mullite B is also stronger at 1000°C, i.e. at the first stage in mullite formation. This fact suggests the initial formation of an Al_2O_3-rich mullite and reflects the change in chemical composition of mullite.

3.2 Thermal analysis

Figure 4 shows DTA curves of samples A, B and C that had been thermal treated at 750°C for 3 h. Sharp exothermic peaks were observed at 989 and 975°C in samples A and B, respectively; whereas two well-defined exothermic peaks were detected in sample C at ~945 and 983°C. XRD analysis of the former samples after the exothermic peaks indicated the presence of mullite as crystalline phase in both samples, whereas for sample C the crystalline phases associated with the first and second exothermic effects were γ-Al_2O_3 and mullite, respectively. In general, the first exothermic peak

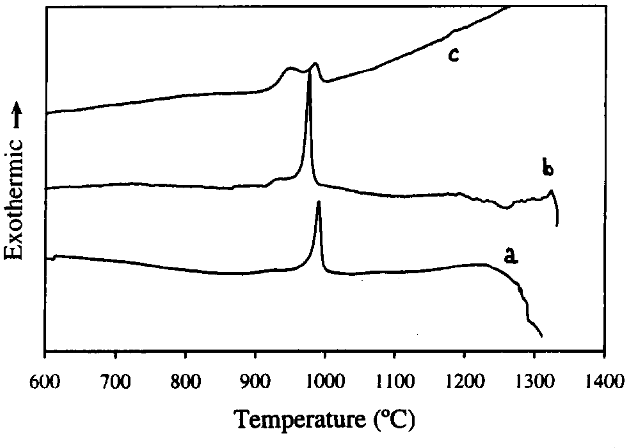


Fig. 4. DTA curves of gel-derived glass powders: (a) sample A; (b) sample B; (c) sample C.

was shifted to lower temperatures for samples with higher alumina content. This tendency was in agreement with previously reported results for systems richer in alumina than composition A.[12,16]

3.3 Thermal evolution of crystalline samples

X-ray diffractograms of samples A, B and C fired at different temperatures are shown in Figs 5, 6 and 7, respectively. At 1000°C the sample of gel A showed mullite as the only crystalline phase. In samples B and C, however, γ-Al_2O_3 was also detected at this low temperature. The amount of γ-Al_2O_3 was very small for the stoichiometric sample B; however, it was the major crystalline phase for sample C. This fact is in agreement with results obtained when the preparation of mullite takes place from a single-phase precursor in which a high degree of chemical homogeneity is reached.[2,17]

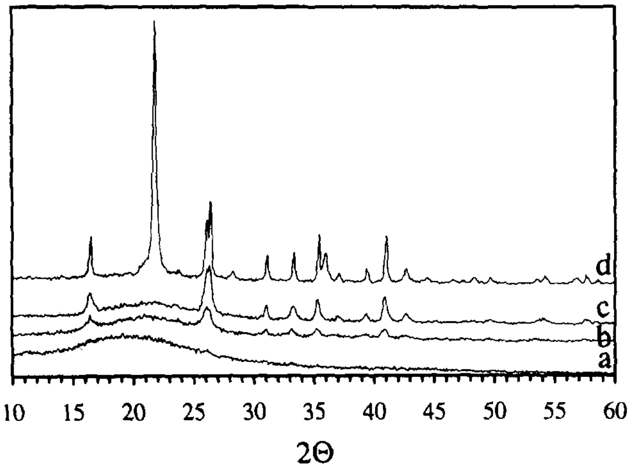


Fig. 5. XRD patterns of sample A gels fired at: (a) 750°C/3 h; (b) 1000°C/15 h; (c) 1200°C/15 h; (d) 1500°C/0.5 h.

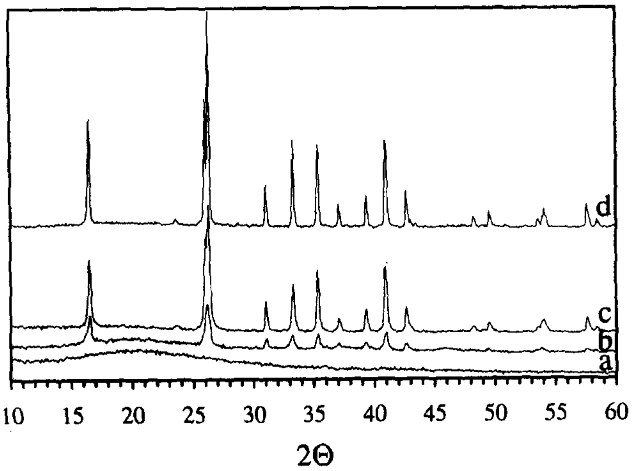


Fig. 6. XRD patterns of sample B gels fired at: (a) 750°C/3 h; (b) 1000°C/15 h; (c) 1200°C/15; (d) 1400°C/15 h.

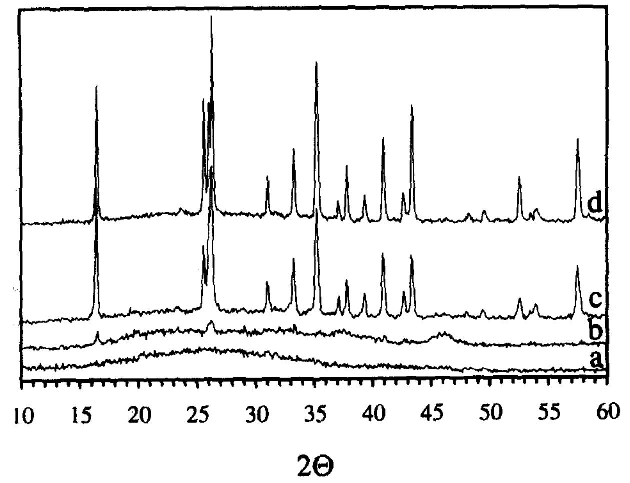


Fig. 7. XRD patterns of sample C gels fired at: (a) 750°C/3 h; (b) 1000°C/15 h; (c) 1200°C/15 h; (d) 1400°C/15 h.

In fact, some doubts about whether gels B and C were single-phase or not could arise. However, the DTA curves for gels B and C indicated that the exothermic peaks could be ascribed to mullite and to γ-Al_2O_3 and mullite, respectively. Reports on mullite formation from diphasic gels have indicated the formation of Al–Si spinel without detecting an exothermic peak around 1000°C and only showed a small rounded peak at ~1250°C associated with the formation of mullite.[18-20] Thus our specimens, which showed mullite and spinel as the crystalline phases at ~1000°C after thermal treatment, could be considered as single-phase gel precursors. The formation of spinel together with mullite has been interpreted in terms of favourable experimental conditions leading to the segregation of alumina and silica in alkoxide-derived gels. The prevention of that alumina–silica segregation, as has been previously reported in the literature,[20] is especially problematic in dual alkoxide systems even for the method of preparation used in this work, in which water was not really added as a separate reagent but was homogeneously distributed in the prehydrolysed TEOS solution before adding the aluminium alkoxide solution.

By increasing the temperature mullite was completely developed in sample B at temperatures as high as 1400°C but cristobalite and corundum were also detected as secondary crystalline phases in samples A and C, respectively. This result was in accordance with the phase diagram for compositions placed on either side of the solid solution limit for mullite.[21] Variation of the lattice parameters of mullite with increasing temperature for samples A, B and C is given in Tables 1, 2 and 3. The change of the parameter *a* as a function of temperaure, i.e. lowering *a* with increasing temperatures, can be related to changes in the mullite composition in accordance with Cameron's results.[5] Thus, mullites formed at the first stage of crystallization were richer in Al_2O_3 than those formed as the calcining temperature was raised. It should be noted that end mullites produced in composition B (3 : 2 as Al_2O_3/SiO_2 molar ratio) between 1400 and 1500°C were as rich in Al_2O_3 as composition C (with 9 : 2 as molar ratio). This fact can be related to the initial formation of a mullite very rich in SiO_2

Table 1. Lattice parameters for sample A fired at different temperatures

Temperature (°C)	a*(Å)*	b*(Å)*	c*(Å)*
1000	7·577 ± 0·016	7·702 ± 0·017	2·8867 ± 0·0023
1200	7·565 ± 0·006	7·692 ± 0·004	2·8829 ± 0·0009
1300	7·551 ± 0·004	7·688 ± 0·002	2·8851 ± 0·0006
1400	7·542 ± 0·003	7·691 ± 0·002	2·8797 ± 0·0005
1500	7·543 ± 0·003	7·690 ± 0·002	2·8806 ± 0·0005
JCPDS 15-776	7·5456	7·6898	2·8842

Table 2. Lattice parameters for sample B fired at different temperatures

Temperature (°C)	a*(Å)*	b*(Å)*	c*(Å)*
1000	7·584 ± 0·006	7·682 ± 0·005	2·8802 ± 0·0010
1200	7·554 ± 0·007	7·686 ± 0·003	2·8828 ± 0·0006
1300	7·553 ± 0·003	7·687 ± 0·002	2·8851 ± 0·0005
1400	7·552 ± 0·003	7·688 ± 0·002	2·8852 ± 0·0005
1500	7·552 ± 0·003	7·690 ± 0·002	2·8852 ± 0·0004

Table 3. Lattice parameters for sample C fired at different temperatures

Temperature (°C)	a*(Å)*	b*(Å)*	c*(Å)*
1000	7·565 ± 0·008	7·690 ± 0·005	2·8845 ± 0·0024
1200	7·554 ± 0·006	7·679 ± 0·005	2·8849 ± 0·0010
1300	7·557 ± 0·003	7·688 ± 0·003	2·8875 ± 0·0008
1400	7·553 ± 0·003	7·685 ± 0·002	2·8840 ± 0·0004
1500	7·552 ± 0·002	7·687 ± 0·002	2·8843 ± 0·0004

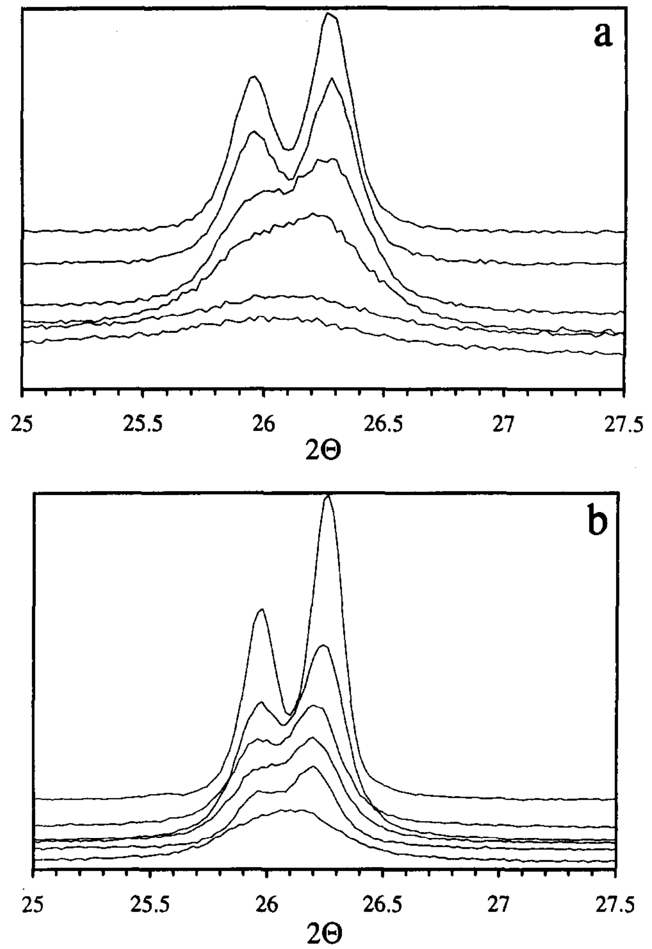


Fig. 8. 1 2 0/2 1 0 reflection pair for powders fired at different temperatures (from 1000 to 1500°C in 100°C intervals) recorded at low goniometer speed: (a) sample A; (b) sample B.

together with the large crystallization of γ-Al_2O_3 in sample C. Further, mullite evolution by solution of α-Al_2O_3 in the SiO_2-rich glassy phase is unfavoured kinetically.

Primarily crystallized mullite at 1000°C could be associated with pseudo-tetragonal mullite because no splitting of peaks with Miller indices of 1 2 0, 2 4 0, 0 4 1 and 2 5 0 was observed. However, the latter could be the result of poor crystallization of mullite and consequently low resolution. Increasing the soaking time led to an initial splitting in the peaks. Likewise, a further increase of calcining temperatures gave rise to a clear angular separation of diffraction lines that was more evident at high temperatures, as displayed in Fig. 8. So it can be considered that the first crystalline phase at 1000°C was pseudo-tetragonal or near orthorhombic and that the phase transformed into a truly orthorhombic one upon increasing either holding time or heating temperature.

The attempt to obtain results related to the controversial occurrence of tetragonal or orthorhombic mullite from sample C, which has an initial composition with $x = 0{\cdot}70$, i.e. (in mol%) 81·8 Al_2O_3, has not been successful. Thus, XRD analysis is of crystalline Al_2O_3-richer mullite obtained by calcining a gel-like glass sample at 1000°C/3 h indicated the formation of orthorhombic mullite with $a < b$, like mullites from samples A and B. However, it was remarkable that sample C was very poorly crystallized at 1000°C even though peaks of mullite were clearly identified. Except at 1000°C, in the overall range of temperature the composition of mullite C was similar to that of mullite B, and is considered to be due to the crystallization of γ-Al_2O_3 at the first step along with poor chemical homogeneity of the precursor gel so that, as consequence, reactivity in the system is very slow. This finding for sample C did not allow us to check the recent results of Schneider *et al.*,[6] which appeared to suggest that mullites very rich in Al_2O_3 were actually orthorhombic instead of tetragonal, as first suggested by Cameron.[5] The former authors have identified mullites with $a > b$, which supposedly must correspond to compositions higher in Al_2O_3 than that corresponding to 79 mol% Al_2O_3. However, this Al_2O_3-rich mullite phase was thermally unstable and above ~1050°C, the lattice parameters gradually shifted back to those of conventional mullite.[6]

3.4 SEM and TEM observations

Figures 9 and 10 display scanning electron micrographs of dried and fired gels of samples A, B and C. As can be distinguished from Fig. 9, large agglomerates with a flat outer surface were present; their fracture surfaces revealed that the agglomerates were made up of small particles. The size of the mullite particles obtained upon heating the amorphous gel particles seemed to be independent of temperature for specimen B, see Fig. 10(b). Also, note that directional growth displayed in particles of specimen C, Fig. 10(c), could be due to the presence of liquid phase. For samples A and C a second phase was observed, characterized by XRD as cristobalite and corundum, respectively.

TEM images of samples A and B are also presented in Figs 11 and 12. Some evidence for the presence of very small particles with size <10 nm is found for the dried gel in Fig. 11. This picture was obtained by deviation from the exact focus condition, and allowed the observation of a fine microstructure that differed somewhat from the irregularly mottled appearance generally associated with fully dense amorphous materials.[22] Examination of sample B at 1500°C showed small, relatively equiaxed particles as displayed in Fig. 12. The particle size of mullite in sample A at 1500°C was the same as that in sample B.

4 Conclusions

Monophasic gels with Al/Si atomic ratios of 2 : 3, 3 : 1 and 9 : 1 were prepared to examine the effect of nominal composition on either mullite formation pathway or microstructural evolution of mullite. Formation of an Si–O–Al network was detected by IR spectroscopy for compositions B and C, while the network present in sample A was built up of Si–O bonds. Al_2O_3-rich mullite was first observed at 1000°C for the three compositions. Full development of mullite took place at 1400°C. On heating the samples, changes in the composition of initial mullites to SiO_2-richer mullite were detected in agreement with the phase diagram. Differences in the compositions of the mullites developed (obtained from lattice parameters) were as expected, except for the case of mullite C which

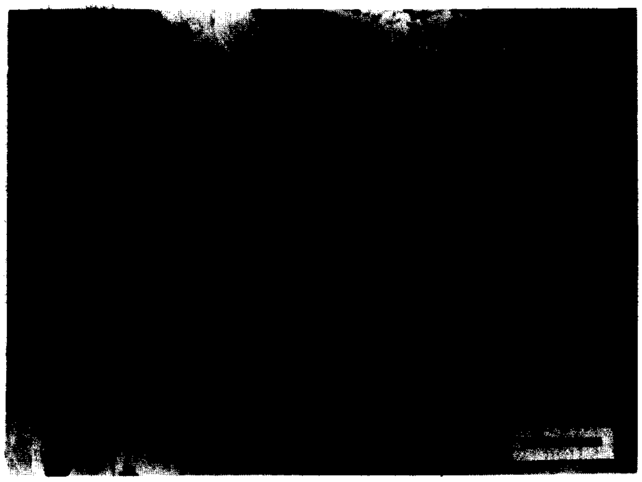
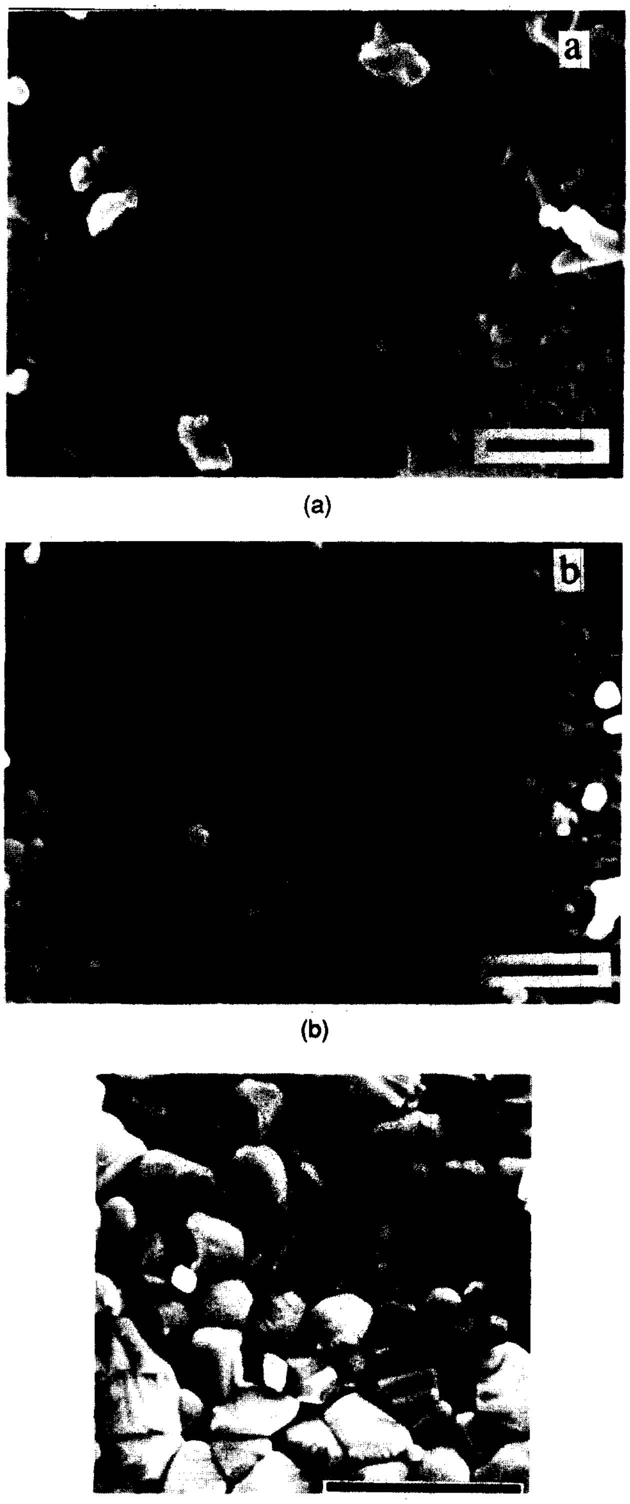


Fig. 9. SEM micrograph of sample B dried gels (120°C/24 h); bar = 5 μm.



(a)

(b)

(c)

Fig. 10. SEM micrographs of powders fired at 1500°C: (a) sample A; (b) sample B; (c) sample C; bar = 1 μm.

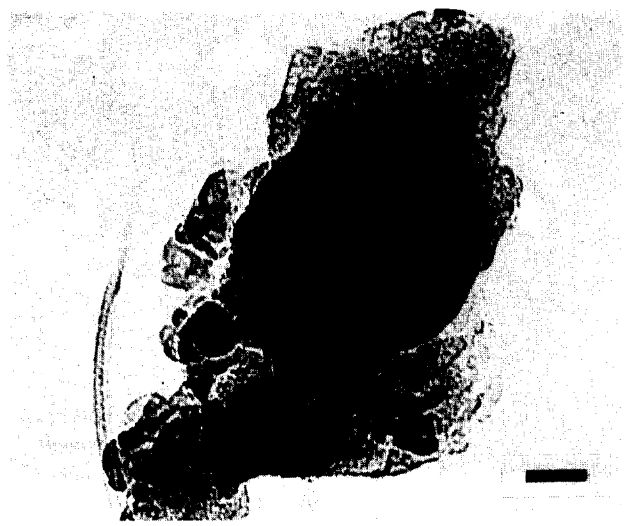


Fig. 11. TEM micrograph of sample B dried gels; bar = 50 nm.

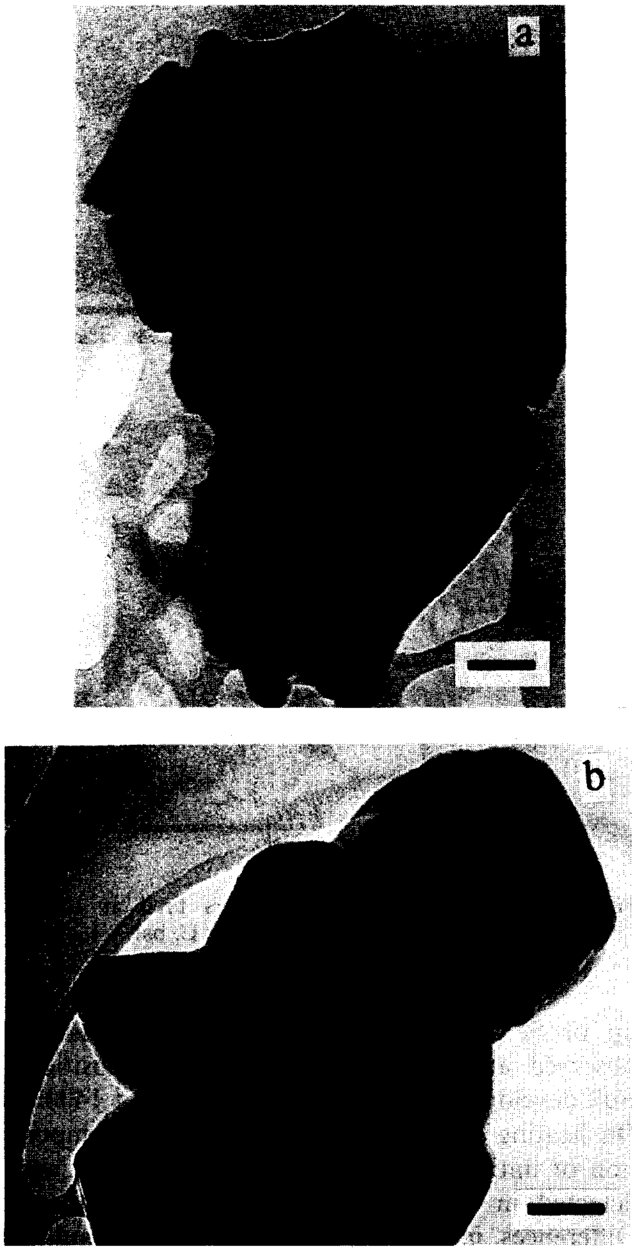


Fig. 12. TEM micrographs of powders fired at 1500°C: (a) sample A; (b) sample B; bar = 50 nm.

seemed to be poorer in Al_2O_3 than mullite B. Microstructural study by SEM indicated that in samples B and C the particle size at higher temperatures is almost constant. However, specimen C displayed a directional growth which was due to presence of liquid phase.

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