

## Mullite Based Compositions Prepared by Sol-Gel Techniques

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**Abstract.** Ceramic powders and gels in the mullite-alumina system with different compositions were prepared by sol-gel method. The preparation of gels was done in strong acidic conditions and also with the addition of ammonia. The powders were prepared by dropping the sols on a hot plate. The effect of water/alkoxide and ethanol/alkoxide ratios was studied together with the type of catalyst used (hydrochloric acid or ammonia). The thermal evolution of materials was followed by thermal analysis, X-ray diffraction, specific surface area measurements and electron microscopy. The morphology of powders was also studied. The characteristic exothermic peak attributed to a good mixing degree of the Al and Si species was observed at  $\sim 980^\circ\text{C}$ . The intensity of this exothermic peak was more pronounced in gels than in sol-gel derived powders. The crystalline phases formed are related with the preparation conditions and with the thermal treatment. The crystallisation of mullite and transient phases of alumina were observed in powder samples heat treated at  $1000^\circ\text{C}$ , while in gel samples mullite was the only crystalline phase detected.

**Keywords:** alumina-silica, mullite, composites, gels and powders

### 1. Introduction

Mullite and mullite-alumina composites are well known as industrial materials for electronic, and high-temperature applications due to their low thermal expansion coefficient, low dielectric constant, high temperature strength creep resistance and good thermal and chemical stability [1, 2]. Several methods have been used to prepare mullite powders. The mullitisation temperature depends on the mixing degree attained by the Al and Si species in the precursors, being as high as  $\sim 1700^\circ\text{C}$  when mixtures of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  powders are reacted [3], and as low as  $\sim 1000^\circ\text{C}$  when the mixing scale in the precursors is at the molecular level [4, 5]. Several sol-gel methods have been used to prepare mullite powders [4–7]. In this study sol-gel based techniques have been used to prepare mullite-alumina gels and powders as part of a study using different preparation procedures for this end [2, 8]. Different procedures were adopted in order to optimise the crystallisation of mullite and mullite-alumina.

### 2. Experimental

Samples with composition  $x\text{Al}_2\text{O}_3 \cdot (100-x)\text{SiO}_2$  ( $x = 60.0$  and  $64.3$  mol%) were prepared using tetraethylorthosilicate (TEOS) and aluminium nitrate nonahydrate as raw materials. Ethanol (absolute) was used to dissolve the nitrate. Two catalysts: ammonia (samples MAG2 and MAP2) and hydrochloric acid, together with two molar ratios water/TEOS were used (Table 1). In order to avoid precipitation, ammonia has to be added together with the water.

For the preparation of gels (samples MG, MAG1, MAG2, MAG3 and MAG4), the clear sols were put in closed containers and kept at  $60^\circ\text{C}$  until gelation occurred. After 7 days at  $60^\circ\text{C}$ , the gels were dried at  $120^\circ\text{C}$  for 48 hours. For the preparation of powders (samples MP, MAP1\*, MAP2, MAP3 and MAP4), the clear sols were dropped on a "hot-plate" ( $\cong 250\text{--}300^\circ\text{C}$ ). Sample MPP was obtained by precipitation of the sol on diluted ammonia followed by successive washing with water and acetone-toluene-acetone.

*Table 1.* Preparation conditions of gels and powders.

Composition (mol%)	Sample	Molar ratio			
		H <sub>2</sub> O/TEOS	HCl/TEOS	NH <sub>3</sub> /TEOS	EtOH/TEOS
60.0Al <sub>2</sub> O <sub>3</sub> .40.0SiO <sub>2</sub>	MG	4.0	0.2	—	39
	MP	4.0	0.2	—	39
	MPP*	4.0	0.2	—	39
64.3Al <sub>2</sub> O <sub>3</sub> .35.7SiO <sub>2</sub>	MAG1	4.0	0.2	—	47
	MAP1*	4.0	0.2	—	47
	MAG2	4.0	—	0.2	47
	MAP2	4.0	—	0.2	47
	MAG3	10.0	0.2	—	47
	MAP3	10.0	0.2	—	47
	MAG4	4.0	0.2	—	94
MAP4	4.0	0.2	—	94	

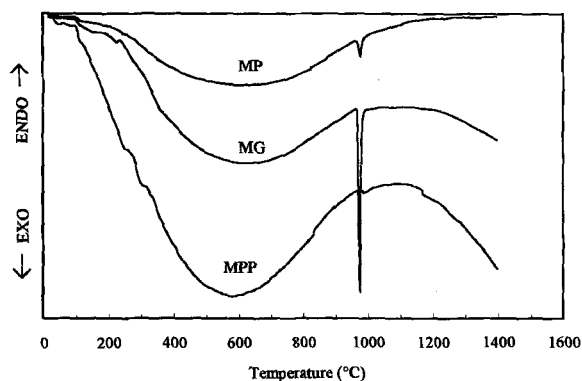
(\*sample MAP1 was prepared by dropping the sol on a fixed hot plate, sample MAP1F, and with rotation of the container, sample MAP1R).

All samples (gels and powders) were heat treated at 500°C and at 1000°C for 2 hours with a heating rate equal to 10°C·min<sup>-1</sup>.

Thermal analysis (DTA and TGA) were simultaneously performed in a computer-controlled LINSEIS/THERMAL instrument at a heating rate of 10°C·min<sup>-1</sup> up to 1400°C to study the changes occurring in the powders during heat treatment. X-ray diffraction (XRD) studies were carried out at room temperature with a computer-controlled Rigaku XDMAX X-ray diffractometer by using CuK $\alpha$  radiation in the 10 to 70° 2 $\theta$  range at a scanning speed of 2° 2 $\theta$ /min. The specific surface area of powders was characterised by nitrogen adsorption (B.E.T. method) using a QuantaSorb Surface Area Analyser-Quanta Chrome Corporation, and the morphology of powders was observed by scanning electron microscopy (SEM), using a Hitachi S4100-1 microscope.

### 3. Results and Discussion

The influence of the synthesis route on the thermal behaviour and on the sequence of phase development for the stoichiometric mullite precursors (MPP, MP and MG) can be observed in Fig. 1 (DTA curves of the dried samples) and Fig. 2 (XRD patterns of the samples calcined at 1000°C). Sample MPP was obtained by rapid hydrolysis and precipitation of the sol on diluted ammonia. Samples MP and MG were prepared in strong acidic conditions. In the first one the



*Figure 1.* Differential thermal analysis diagrams obtained for samples with the stoichiometric mullite composition.

clear sol was dropped on a “hot-plate” ( $\cong 250\text{--}300^\circ\text{C}$ ), while the MG precursor was prepared by slow sol-gel transition (7 days at 60°C). It can be seen that both the thermal evolution and the phase transition are rather dependent on the synthesis route adopted. The DTA curve of the sample MG shows a strong exothermic peak at about 975°C. Mullite is the only identifiable phase in the powder heat treated at 1000°C (Fig. 2). These characteristics mean that the chemical homogeneity achieved in the MG precursor is at the molecular level [4, 5]. The exothermicity of the peak at 975°C decreases when the powder was obtained by rapid evaporation of the clear sol drops in contact with the hot-plate. The correspondent XRD

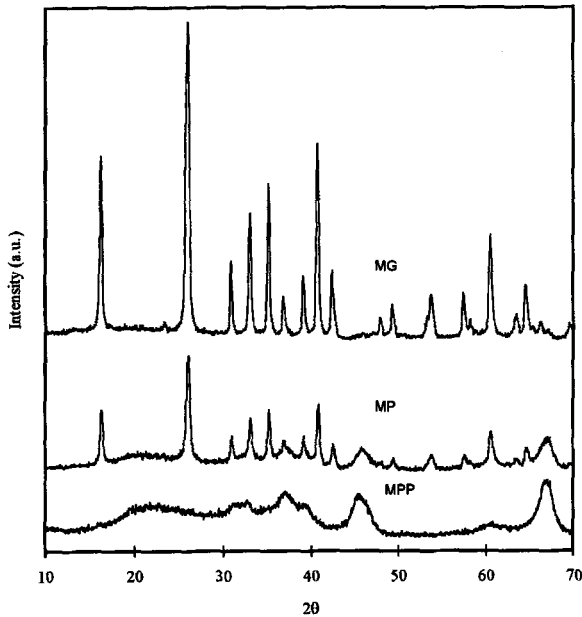


Figure 2. XRD patterns obtained for samples with the stoichiometric mullite composition heat treated at 1000°C for 2 hours.

pattern shows that  $\gamma$ - $\text{Al}_2\text{O}_3$  or spinel phase were also formed, together with a less well defined mullite. A broad and relatively intense exothermic peak extending from 300°C to 900°C and a very small exothermic peak observed at about 985°C are the main features of the DTA curve of the sample MPP. The first one has been attributed to the crystallization of transient alumina phases and the condensation of the amorphous silica phase [9–11], while the second is due to the crystallisation of both  $\gamma$ - $\text{Al}_2\text{O}_3$  and spinel phase [12, 13, 16]. The XRD diagram of this sample calcined at 1000°C exhibits the characteristic peaks of the  $\gamma$ - $\text{Al}_2\text{O}_3$ . Traces of  $\theta$ - $\text{Al}_2\text{O}_3$  are also present. So, MG behaves as a single phase precursor while the MPP is clearly diphasic in character. Relatively to these samples the MP represents an intermediary situation. These results seem to confirm the model of Okada and Otsuka according to which a decreasing segregation scale favours the mullite crystallisation [14].

The effects of the synthesis route on the thermal behaviour and on the microstructure evolution of composite precursors are compared in Figs. 3 and 4, respectively. The DTA of the MAG1 sample is identical to that of the MAPR1. Both precursors MAP1F and MAP1R were prepared by dropping the clear sol on a hot-plate, which was maintained fixed (MAP1F), or rotate

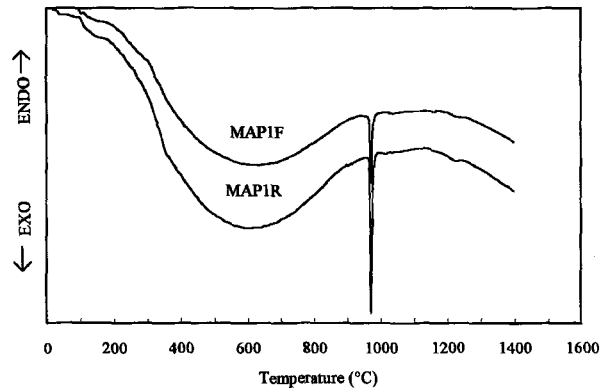


Figure 3. Differential thermal analysis diagrams obtained for samples in the mullite-alumina system.

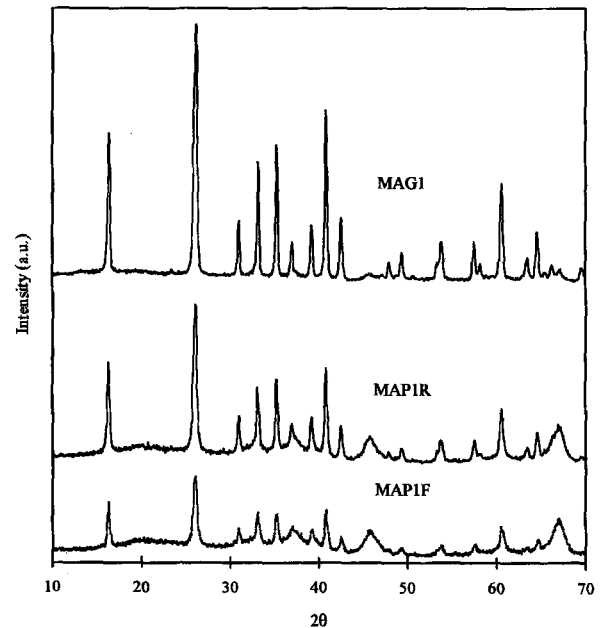
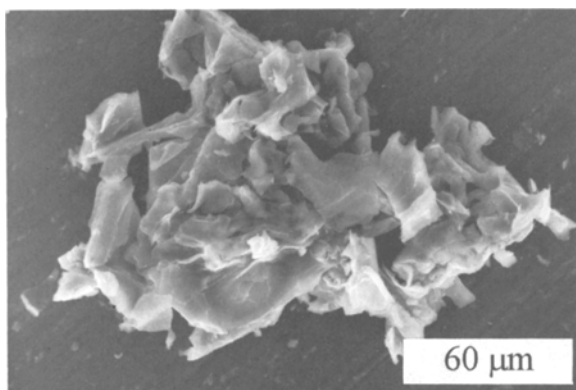


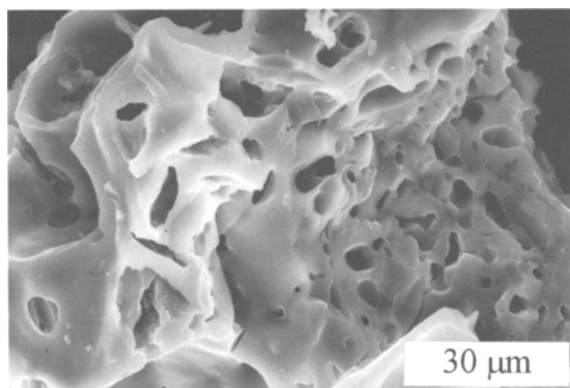
Figure 4. XRD patterns obtained for samples in the mullite-alumina system heat treated at 1000°C for 2 hours.

(MAP1R) in order to avoid two successive drops to fall on the same area. MAG1 was obtained by slow sol-gel transition (7 days at 60°C). It can be observed that in spite of the excess of alumina present in these precursors, well crystallized mullite was the only identifiable phase formed at 1000°C in the MAG1. This might be attributed its high chemical homogeneity and to the small difference between this composition and that correspondent to the high alumina side of the mullite solid

solution [15, 17, 18]. The other two samples show the presence of both  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and mullite. The transformation to mullite was more extensive or its crystallinity was improved when the hot-plate was rotated. This increase in XRD intensity peaks observed in Fig. 4 is consistent with the differences in the exothermicity of these reactions occurring at 975°C, as shown in Fig. 3. The endothermicity of the evaporation process lowers locally the temperature of the hot-plate and increases the time necessary to transform the solution into a powder. The rotation of the hot-plate can mitigate this drawback by continually exposing new hot zones to the falling drops. A better approach seems to be the reduction of the size of droplets by spray-drying, as was shown by Jaymes and Douy [5]. In the other gel samples (MAG2, MAG3 and MAG4) mullite crystallization was seen to be independent of the preparation conditions of sols



(a)



(b)

Figure 5. Scanning electron microphotographs of sample MAP1 as-prepared 5(a) and heat treated at 500°C for 2 hours 5(b).

(molar ratios water/TEOS and Ethanol/TEOS and type of catalyst used). In fact all gels present well defined crystallization peaks due to mullite.

For the powder samples MAP2, MAP3 and MAP4 the crystalline phases are not so well defined and are related with the preparation conditions of sols. The formation of mullite in these samples is more intense for powders prepared with lower water content and strong acidic conditions. It was also observed that the raise in ethanol content together with acid content enhances the crystallization of mullite. In all the powders the incipient crystallization of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\theta$ -Al<sub>2</sub>O<sub>3</sub> is also observed.

Specific surface area was measured in powders MP, MAP1 and MAP3. An average value of  $\sim 105$  m<sup>2</sup>·g<sup>-1</sup> was obtained for powders heat treated at 500°C (2 hours) that after 2 hours at 1000°C reduces to  $\sim 14$  m<sup>2</sup>·g<sup>-1</sup>. The microphotographs of powder MAP1 obtained for the powder as-prepared (Fig. 5(a)) and after 2 hours at 500°C (Fig. 5(b)) present the typical morphology of the powders prepared in this study. The as-prepared powders are formed by aggregates that after heat treatment at 500°C (2 hours) present a high porosity due to the liberation of residual organics.

#### 4. Conclusions

For the two compositions of the silica-alumina system studied, mullite formation is favored and with well defined X-ray diffraction peaks, for samples prepared as gels independent of the preparation conditions of the sols. These preparation conditions were more relevant in samples prepared as powders. In fact, in powders obtained from sols prepared in strong acidic conditions and with lower water content or with higher content in ethanol, incipient mullite crystallization is favored. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\theta$ -Al<sub>2</sub>O<sub>3</sub> phases are also observed for powder samples.

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