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Al_2TiO_5 Preparation Starting with Reactive Powders Obtained by Sol–Gel Method

Maria Zaharescu,[a]* Maria Crisan,[a] D. Crisan,[a] N. Drăgan,[a] A. Jitianu[a] and Maria Preda[b]

[a]Institute of Physical Chemistry-Romanian Academy, Bucharest, Romania
[b]University 'Politehnica' Bucharest, Romania

Abstract

Individual Al_2O_3, TiO_2 and SiO_2, as well as binary Al_2O_3–TiO_2 powders have been obtained by sol–gel method, polymeric route. The obtained powders have been characterized by X-ray diffraction (XRD), IR-spectrometry and transmission electron microscopy (TEM) methods. In the used experimental conditions amorphous, submicronic, monodisperse powders have been obtained. The preparation of Al_2TiO_5 and of some compositions situated in the Al_2TiO_5–$Al_6Si_2O_{13}$ pseudobinary system has been realized by solid-state reaction starting with the mentioned above powders. The thermal treatment schedule of the pressed powder mixtures has been established according to the results of differential thermal and thermogravimetric analysis (DTA/TGA). The formation of the compound has been followed by XRD, dimensional variation of the samples and apparent density measurements. The results obtained starting with reactive powders have been compared with those obtained starting with commercial powders. The samples have shown a high reactivity and the formation of tialite was enhanced. However the sintering tendency was not essentially increased. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

Tialite represents a highly appreciate compound due to its very low thermal expansion coefficient. The ceramics containing tialite have a very high thermal shock resistance.[1] Tialite is a compound with an orthorhombic structure with the following lattice parameters: $a = 3{\cdot}591$, $b = 9{\cdot}429$ and $c = 9{\cdot}636$ Å. The density determined by X-ray diffraction is $3{\cdot}70\,g\,cm^{-3}$. Tialite monocrystals present anisotropy, their thermal expansion coefficient ranging between $(+3)$–$(-19)\times10^{-7}\,K^{-1}$. Due to the mentioned anisotropy at the limits between the grains microcrakes occur.[2] As a result of the two mentioned phenomena the tialite based ceramics has a very good thermal shock resistance but low breaking resistance.[3,4] To improve the mechanical resistance of tialite based ceramics the crystal dimensions should be in the microns range and the cooling of the thermally treated sample should be realized with a controlled rate of about $6°C\,min^{-1}$, starting with the sintering temperature.[5] Tialite has an equivalent density lower than the density of the starting materials, that explain the low tendency to sintering of the tialite.[1,6] The solid state reactions of tialite formation are slow and depend on the method of preparation. Moreover tialite undergoes an eutectoidic decomposition. The temperature range in which this phenomenon occurs is very controversially. The phase equilibrium diagrams show that 1200°C is the temperature at which tialite becomes thermodynamically unstable.[7]

Kato *et al.*[8] prepared homogeneous non-crystalline mixtures of alumina and titania by chemical precipitation. By thermal treatment they noticed that first the XRD lines of anatase occur. Further anatase transforms to rutile and finally α-alumina crystallizes. At low heating rate the formation of β-tialite is hindered due to the alumina and respectively rutile crystallization, which precedes the solid state reaction between oxides. At high rate thermal treatment the formation of tialite was noticed at 1250°C. By XRD the authors have determined the equilibrium of eutectoidic reaction at 1281°C. To hinder the eutectoidic dissociation and to improve the sintering tendency the influence of several additives as SiO_2, ZrO_2, MgO, Fe_2O_3, etc.,[3,9,10] have been studied.

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*To whom correspondence should be addressed.

Jambazov and Lepkova[3] have prepared tialite using the sol–gel method. By thermal treatment they noticed that first anatase crystallize at about 650–750°C, then rutile is formed. Between 800–900°C the presence of α-alumina was observed. The tialite formation takes place at temperatures over 1200°C, by the solid state-reaction of the components in crystalline state. Okamura *et al.*[11] have studied the preparation of a composite material by deposition of titanium dioxide layer on the α-alumina surface by the hydrolysis of titanium–isopropilate. The DTA/TG analysis of a mixture with 1:1 Al_2O_3:TiO_2 molar ratio has shown several thermal effects. Between 90 and 250°C an endothermic effect was assigned to the evolution of adsorbed water. Between 370 and 480°C an exothermic effect was assigned to the burning out of the organic residues. The endothermal effect observed in the 1350–1410°C temperature range was assigned to the tialite formation. However, by XRD the tialite formation was noticed at lower temperature, at about 1320°C.

In the present work the preparation of Al_2TiO_5 starting with reactive powders obtained by sol-gel method was studied. The influence of SiO_2 addition on sintering properties was also approached.

2 Experimental

2.1 Synthesis of the reactive powders

The composition of the starting solutions and the experimental conditions used for the individual powders preparation are listed in Table 1. In all cases the hydrolysis was realized with water excess. Base catalysis was used in the case of silicon dioxide preparation.[12] Aluminium[13,14] and titanium oxides[15] formation took place in un-catalysed reaction mixtures. The composition of starting solutions and the experimental conditions used for binary Al_2O_3–TiO_2 powders preparation[8,16] are listed in Table 2.

2.2 Characterization of the reactive powders

The starting oxide powders, as well as thermally treated samples were characterized by XRD, IR method, ATD/TGA and TEM observation. The X-ray diffraction patterns were recorded with a HZG-3 diffractometer using Co K_α radiation. IR spectra were recorded in 4000–200 cm^{-1} range. A Carl Zeiss Jena-Specord M-80 IR equipment was used. The thermal behaviour of the obtained powders was studied by DTA/TGA up to 1400°C in air with Al_2O_3 as reference. A MOM OD-103 Derivatograph with a heating rate of 7·5°C min^{-1} was used.

Table 1. Composition of starting solutions and experimental conditions for individual oxides preparation

Sample	*Molar ratio*			*pH*	*Conditions of reaction*	
	$\frac{C_2H_5OH}{M(OR)_4}$	$\frac{H_2O}{M(OR)_4}$	$\frac{NH_4OH}{M(OR)_4}$		*T(°C)*	*t(h)*
SiO_2[a]	54·6	30	2	8·5	25	6
AlO(OH)[b]	—	100	—	6·5	80	1
TiO_2[c]	85	5	—	5·5	25	0·5

[a] $M(OR)_4 = Si(OC_2H_5)_4$.
[b] $M(OR)_4 = Al(OiC_3H_7)_3$.
[c] $M(OR)_4 = Ti(OC_2H_5)_4$.

2.3 Synthesis of the ceramic masses

The compositions of the synthesized ceramic masses are presented in the Table 3.

The powders were wet homogenized and dried to constant weight. By uniaxial pressing at 400 dN cm^{-2}, 10 mm high samples have been obtained. The samples were fired at temperature between 1250 and 1450°C, with 2 h plateau at the highest temperature; the cooling was made with the furnace. On the obtained samples the phase composition and the sintering tendency were determined. The amount of tialite formed at different temperatures was determined by XRD. The intensities of XRD lines were normalized by the relation:

$$X(\%) = \frac{100 I_x}{I_{Al_2O_3} + I_{\text{cristobalite}} + I_{TiO_2} + 4{\cdot}55 I_{\text{quartz}} + 2 I_{\text{Mulite}} + 2{\cdot}38 I_{\text{Tialite}}}$$

where I represents the intensity of following lines: (101) for TiO_2-rutile; (113) for α-Al_2O_3; (100) for α-quartz–SiO_2; (101) for α-cristobalite–SiO_2; (020) for Al_2TiO_5; (110) for $Al_6Si_2O_{13}$.

On the samples thermally treated the ceramic properties were determined: the linear shrinkage and the density.

The linear shrinkage was determined by measuring the diameter of samples before and after thermal treatment. The density was determined by hydrostatic method.

3 Results and Discussion

3.1 Reactive powders

The individual powders obtained according to the conditions presented in Table 1, are all amorphous, as determined by XRD.

It is well known that powders obtained by sol–gel method contain always adsorbed and structural water, as well as organic residues. The evolution of the mentioned components at different temperatures is obtained by DTA/TGA. The DTA/TGA curves of the individual oxides observed are

Table 2. Composition of starting solutions and experimental conditions for binary Al_2O_3–TiO_2 oxides preparation

Sample	*Alkoxide type*	*Molar ratio*			*pH of the mixture*	*Conditions of reaction*	
		$\frac{ROH}{\Sigma alkoxides}$	$\frac{H_2O}{\Sigma alkoxides}$	$\frac{AcH^c}{\Sigma alcoxides}$		*T(°C)*	*t(h)*
AT1	$Al(O\text{–}tC_4H_9)_3 + Ti(O\text{–}C_4H_9)_4$ molar ratio Al_2O_3:TiO_2 = 1:1	75[a]	7·40	0·61	3·5,4	100	1 in N_2
AT2	$Al(O\text{–}iC_3H_7)_3 + Ti(O\text{–}iC_3H_7)_4$ molar ratio Al_2O_3:TiO_2 = 1:1	75[b]	7·40	—	5·5,6	70	1 in N_2

[a] R = -iC_4H_9;
[b] R = -iC_3H_7;
[c] AcH = acetic acid 10%.

presented in Fig. 1. In all cases the endothermic effects assigned to the evolution of adsorbed water and alcohol is observed. The structural water is eliminated in the 150–400°C temperature range. The water elimination in the case of aluminium oxide takes place in two steps, the second one being accompanied by the endothermal effect at 460°C. The thermal behavior of aluminium oxide powder is characteristic to pseudo-boehmite decomposition.

The exothermic effect, without mass loss, at about 675°C, noticed in the DTA/TGA curve of TiO_2 powder is assigned to the anatase→rutile transformation.

Further characterization of the powders was made both on initial and thermally treated samples at 300°C for SiO_2 and TiO_2 and at 450°C for AlO(OH), respectively.

The IR spectra of the mentioned powders are presented in Fig. 2. In all cases the characteristic vibrations due to the presence of molecular water and structural OH^-, as well as those due to M–O bonds are observed.[17] In the case of aluminium oxide powder, although the XRD shows an amorphous structure, the IR spectrum indicates a higher degree of ordering. After the low temperature thermal treatment, mentioned above, the IR vibrations due to the molecular water decrease and the vibrations due to the M–O bonds increase.

The TEM micrographs of the initial and thermally treated powders are presented in Fig. 3. In all cases monodisperse particles in micron range have been obtained. The dimension of the particles increases from $Al_2O_3 < SiO_2 < TiO_2$. After the thermal treatment the dimensions of the particles do not changes, but the aggregation tendency of the particles decreases.

The binary Al_2O_3–TiO_2 powders, are also amorphous as determined by XRD. The IR spectra of the powder AT1 are presented in Fig. 4. Compared to the IR spectra of AlO(OH) and TiO_2

Table 3. Composition of synthetized samples

Sample	*Phase composition (%)*		*Starting oxides*
	AT	A_3S_2	
1	100	—	Commercial oxides
2	100	—	Individual oxides obtained by sol–gel method
3	100	—	**a** Binary oxides obtained by sol–gel method (route AT1) **b** Binary oxides obtained by sol–gel method (route AT2)
4	50	50	**a** Commercial oxides **b** Individual oxides obtained by sol–gel method
5	75	25	**a** Commercial oxides **b** Individual oxides obtained by sol–gel method
6	25	75	**a** Commercial oxides **b** Individual oxides obtained by sol–gel method

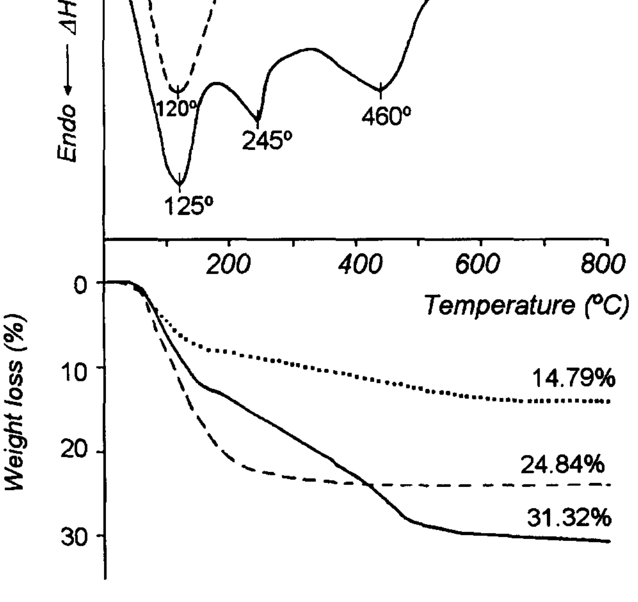

Fig. 1. DTA/TGA curves of individual oxides obtained by sol–gel method.

individually prepared, much broader bands are observed. That could be explained by formation of Al–O–Ti bonds.

The DTA/TGA curves presented in Fig. 5, show the endothermic effects at about 180°C assigned to water evolution followed by other three exothermic effects at about 450°C due to the burning out of organic residues and at about 750 and 960°C, respectively, assigned to the rutile and α-alumina crystallization. According to the previous results of

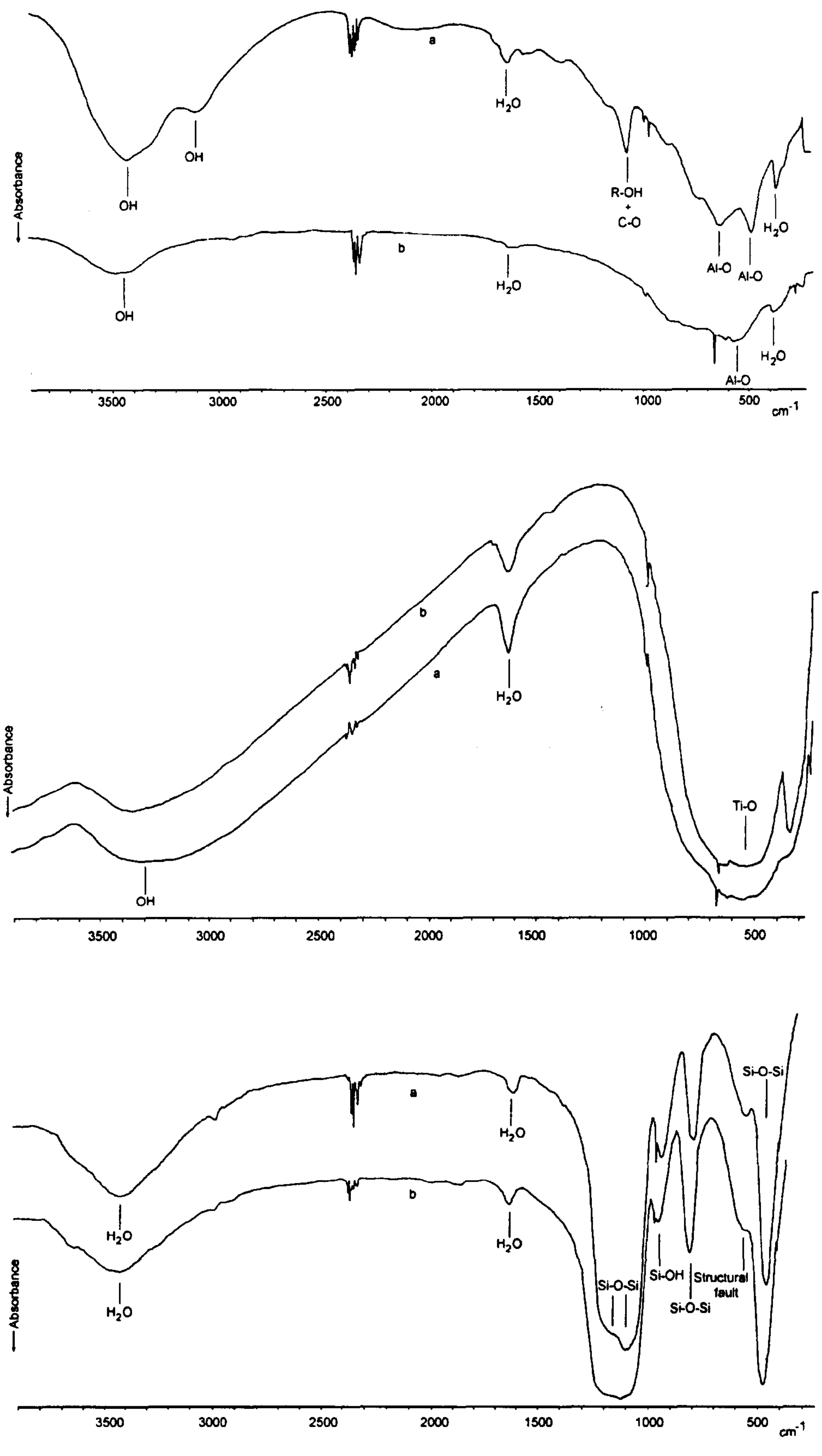

Fig. 2. IR spectra of individual oxides obtained by sol–gel method.

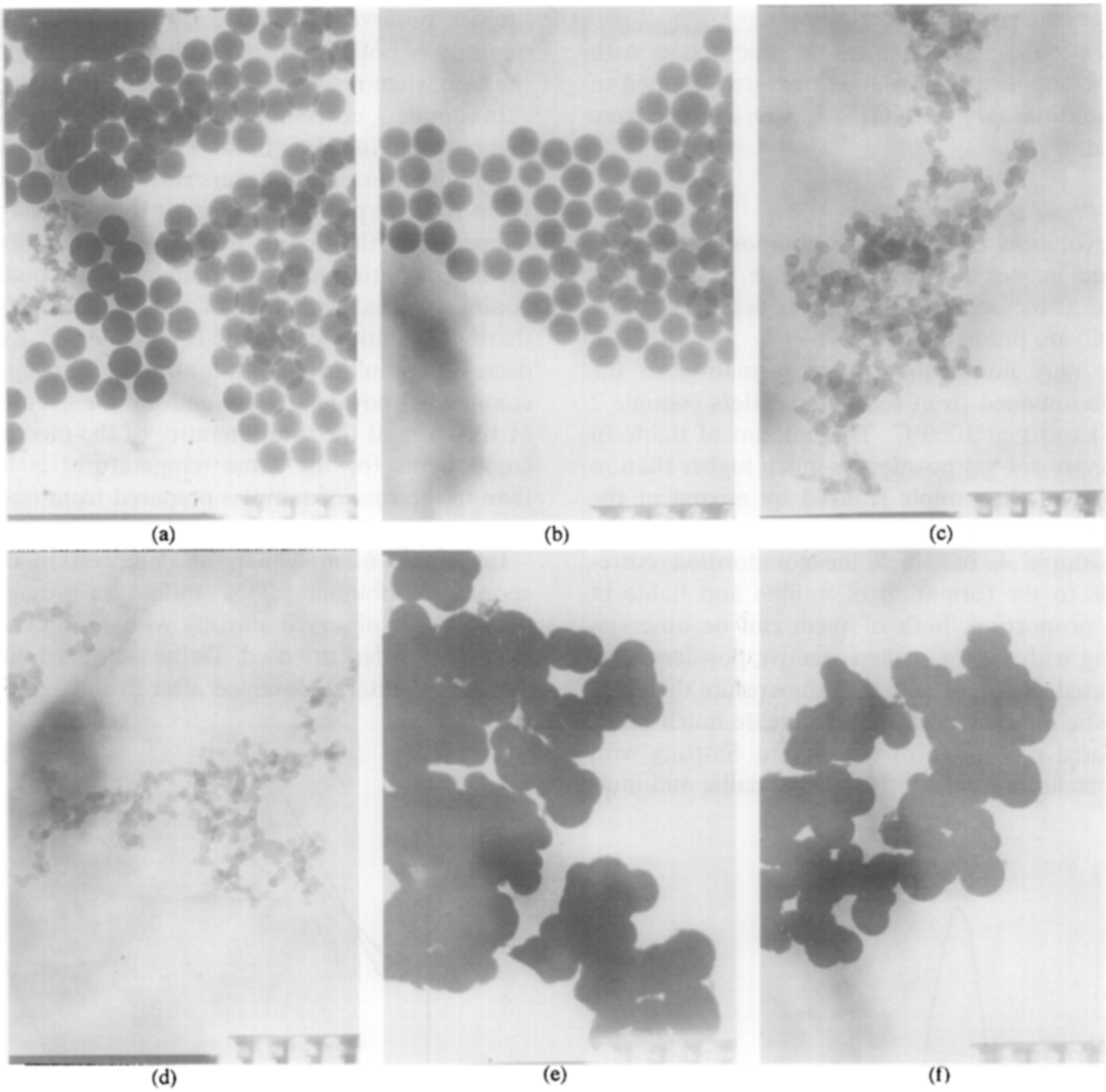

Fig. 3. TEM micrographs of the individual oxides obtained by sol–gel method.

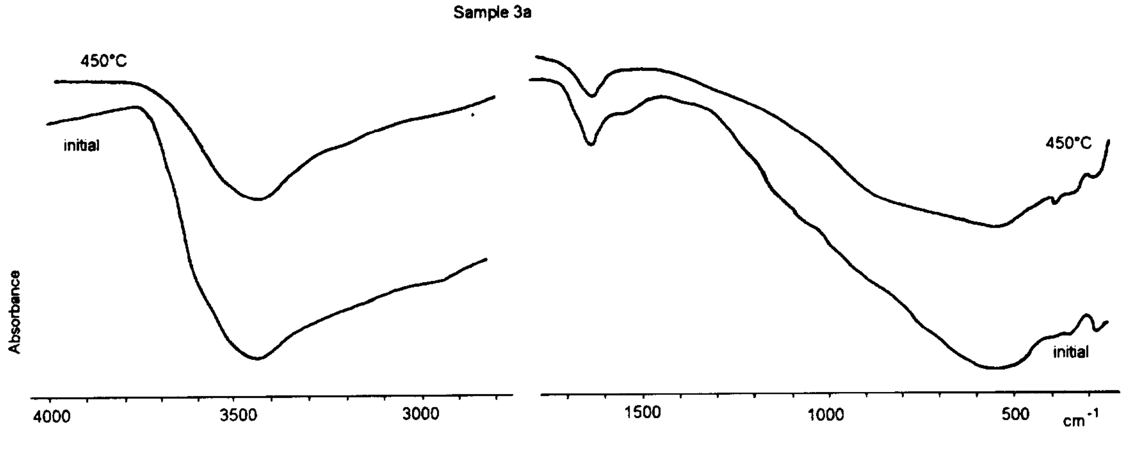

Fig. 4. IR spectra of the binary Al_2O_3–TiO_2 powders obtained by sol–gel method (route AT1).

Kato *et al.*,[11] the endothermic effect at about 1350°C can be assigned to tialite formation, in non-isothermal conditions.

The DTA/TGA curves of the mixture of tialite composition obtained from the individual oxides exhibit only a small exothermic effect assigned to α-alumina crystallization (Fig. 5).

It becomes clear that the binary sol–gel powders are much more reactive than the mixture obtained from individually obtained powders.

3.2 Ceramic masses

As mentioned in the Table 3 ceramic masses with tialite composition as well as mixtures situated in the pseudo-binary Al_2TiO_5–$Al_6Si_2O_{13}$ system were studied.

3.2.1 Phase composition

The evolution of the phase composition of the ceramic masses presented in Table 3, thermally treated at temperatures ranging between 1250 and 1450°C, are presented in Figs 6–9.

One may notice that tialite formation in the sample obtained from reactive powders (sample 2 and 3) starts at 1250°C. The amount of tialite in the binary sol–gel powders is much higher than in the case of the sample realized by mixing of the individual sol–gel powders (Fig. 6).

In sample 4, in which the composition corresponds to the formation of mullite and tialite in equal proportion, both of them can be observed starting with 1250°C, when reactive powders have been used. By increasing the temperature the characteristic XRD lines of tialite increase much faster compared with those of the mullite. Starting with commercial powders, although the tialite and mullite are observed only at 1350°C, at 1450°C the quantity of both tialite and mullite is higher than in the case when reactive powders were used (Fig. 7).

In sample 5, corresponding to a theoretical phase composition of 75% tialite + 25% mullite, tialite and mullite formation occurs starting with 1250°C, when reactive powders are used. By increasing the temperature the tialite quantity in the mixture increases continuously. Although mullite quantity is almost equal with that of tialite at 1250°C the thermal evolution of mullite is much lower. Even a decrease of mullite amount is noticed. Starting with commercial powders tialite and mullite occur only at 1350°C and the total quantity of the mentioned components for the same temperatures is lower than in the case of samples prepared from reactive powders (Fig. 8).

In sample 6, in which the composition corresponds for obtaining 75% mullite its progressive formation is observed starting with 1250°C, when reactive powders are used. Tialite is noticed only in the X-ray patterns obtained after firing at 1450°C.

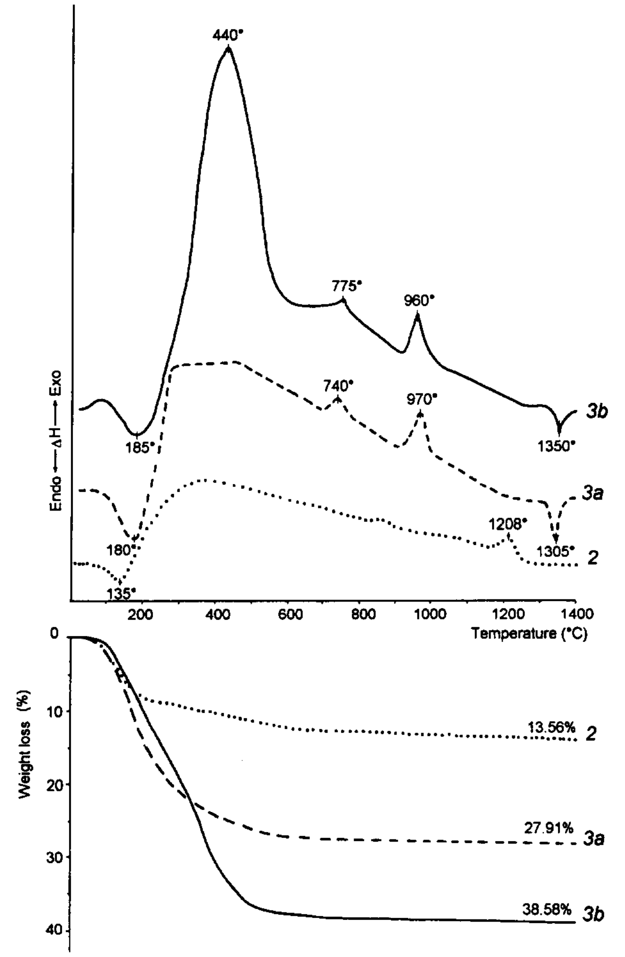

Fig. 5. DTA/TGA curves of binary Al_2O_3–TiO_2 powders obtained by sol–gel method.

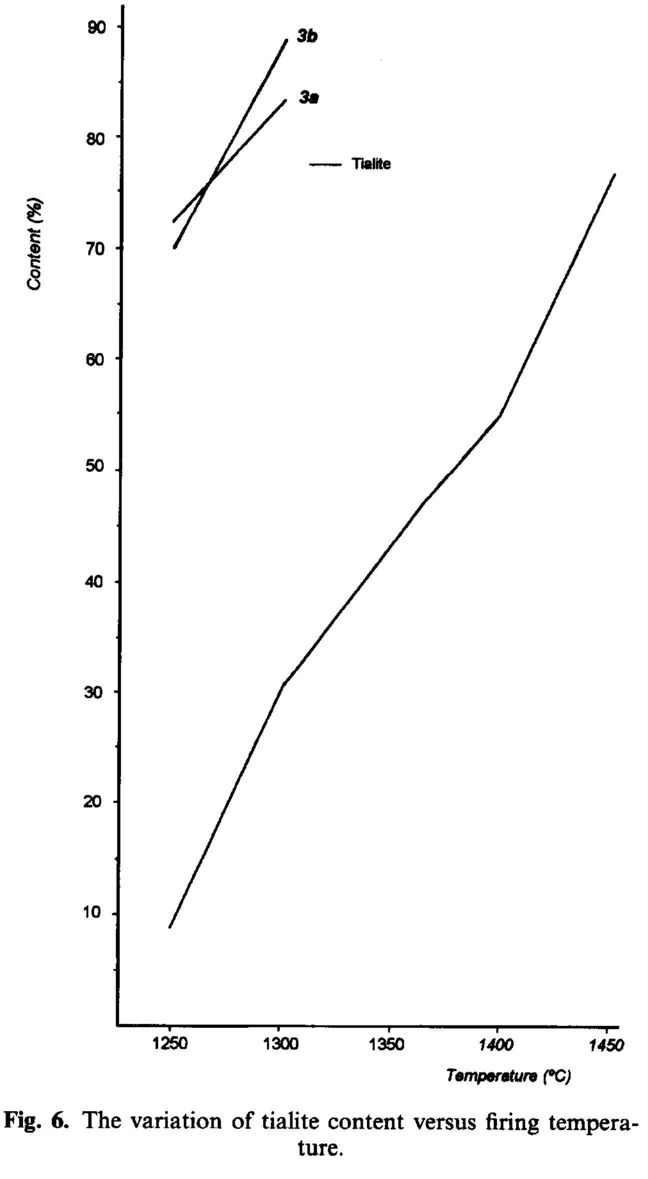

Fig. 6. The variation of tialite content versus firing temperature.

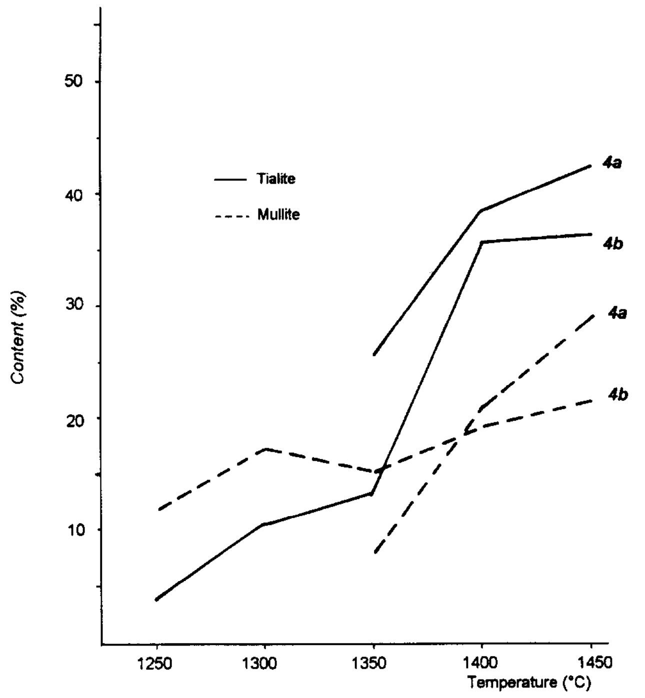

Fig. 7. The variation of tialite and mullite versus firing temperature in sample 4 (50% tialite + 50% mullite).

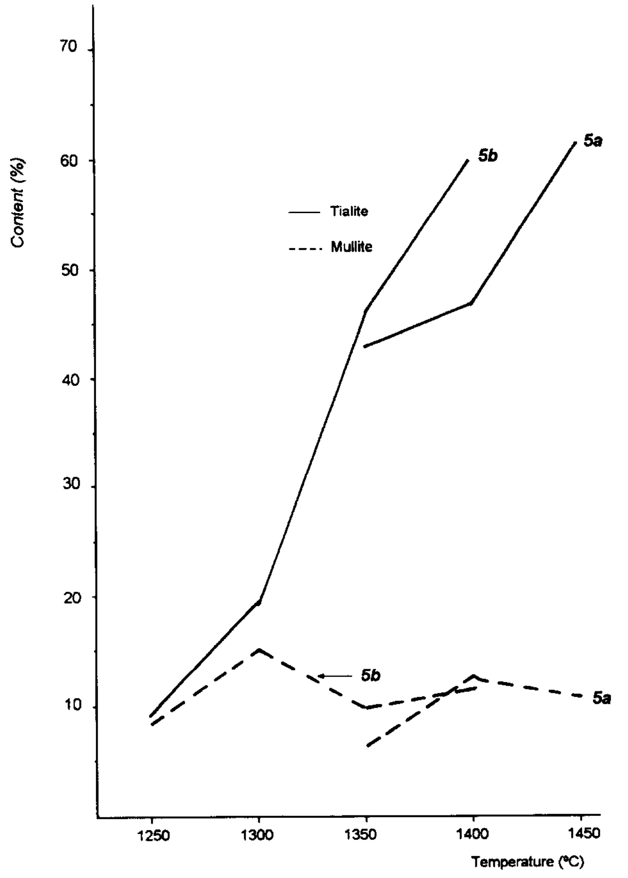

Fig. 8. The variation of tialite and mullite versus firing temperature in sample 5 (75% tialite + 25% mullite).

On may assume that in this case at lower temperatures the TiO_2 reactive powder has catalyzed the mullite formation. Using commercial powders tialite and mullite occur at 1350°C, at 1450°C the quantity is lower than in former case (Fig. 9).

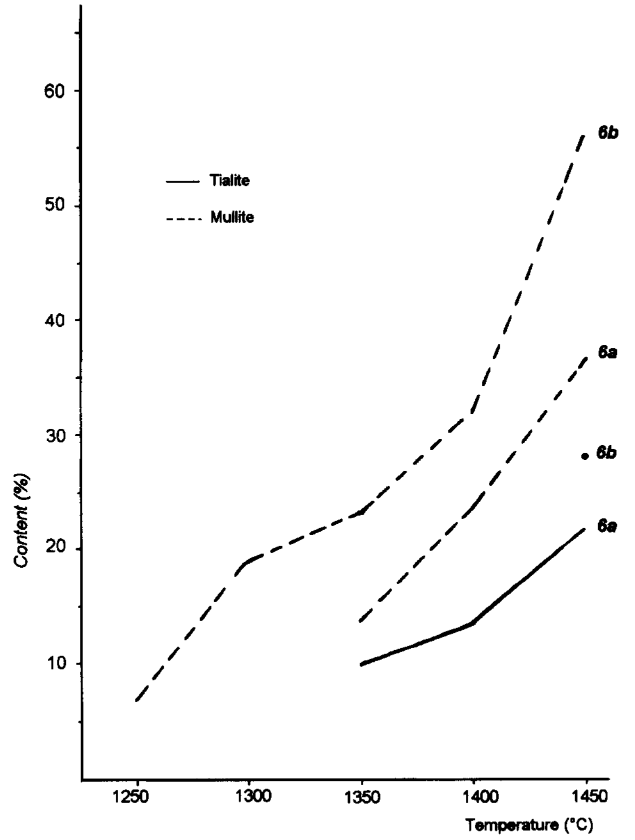

Fig. 9. The variation of tialite and mullite versus firing temperature in sample 6 (25% tialite + 75% mullite).

Table 4. Ceramic properties of tialite based ceramics obtained from reactive powders

Temperature (°C)	*Tialite*		*75% tialite + 25% mullite*	
	Shrinkage (%)	*Density ($g\,cm^{-3}$)*	*Shrinkage (%)*	*Density ($g\,cm^{-3}$)*
1250	—	—	17·07	2·53
1300	21·3	2·80	17·89	2·55
1350	21·3	2·66	18·70	2·63
1400	21·3	2·55	18·70	2·60
1450	18·03	2·33	17·60	2·59

Table 5. Ceramic properties of tialite based ceramics obtained from commercial powders

Temperature (°C)	*Shrinkage (%)*	
	Tialite	*75% Tialite + 25% Mullite*
1250	9·7	6·1
1300	12·1	7·4
1350	8·7	7·5
1400	6·8	7·3
1450	5·0	3·4

3.2.2 Sintering tendency

The sintering tendency has been established by measuring the relative density and the linear shrinkage of the samples fired at the temperatures which range between 1250–14 500°C.

The results obtained starting with reactive powders are presented in Table 4 and the results obtained starting with commercial powders are presented in Table 5.

The linear shrinkage is much higher in the case of the samples obtained starting with reactive powders. However the final density is relatively low. The decreasing of density with increasing of temperatures is explained by tialite formation that has a lower density than the initial oxides.

4 Conclusions

Individual SiO_2, TiO_2, Al_2O_3 and binary TiO_2, Al_2O_3 powders have been prepared by sol–gel method. The powders are amorphous, monodisperse and present a high reactivity. The reactivity of binary TiO_2, Al_2O_3 powder is higher compared to the mixtures prepared from the individual corresponding oxides. All powders also exhibit a high tendency to crystallize. Due to the high reactivity of the powders obtained by sol–gel method the tialite and mullite formation takes place in the studied ceramic masses starting with 1250°C. However the sintering tendency was not essentially increased. Further investigations are underway in order to improve the sintering tendency, by preparing three component ceramic powders by sol–gel method and by using a double firing procedure.

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