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ScienceDirect
Journal of the European Ceramic Society 27 (2007) 2655–2663
www.elsevier.com/locate/jeurceramsoc

Low-temperature Ti-containing 3:2 and 2:1 mullite nanocrystals from single-phase gels

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Received 25 June 2006; received in revised form 13 September 2006; accepted 24 September 2006
Available online 15 November 2006

Abstract

TiO_2-containig single-phase gels with $(Al_2O_3 + TiO_2)/(SiO_2)$ molar ratios 3/2 and 2/1 were prepared by gelling mixtures of aluminium nitrate, tetraethylorthosilicate and titanium isopropoxide. Gels were fast heated at several temperatures up to 1100 °C. Dried and heated gels were characterized by differential thermal analysis (DTA), magic angle spinning nuclear magnetic resonance (MAS-NMR), X-ray powder diffraction (XRD), and scanning and transmission electron microscopies (SEM and TEM). Coupled DTA and XRD results of gels fast heated at 900 °C showed the crystallisation of two mullites as well as a small amount of alumina-silica spinel. ^{27}Al NMR spectra showed the formation of pentacoordinated aluminium before mullite crystallization. The increase of lattice parameters of single-phase mullites heated at 1100 °C indicated that the amount of TiO_2 incorporated into the mullite structure increased on raising the amount of nominal TiO_2 in both series. SEM and TEM images of heated gels at 1100 °C displayed the formation of well-shaped parallelepiped of titanium-doped mullite nanocrystals with crystalline anisotropy.

Keywords: Sol–gel processes; Microstructure-final; Mullite; Solid solution

1. Introduction

Mullite is a very important material due to its thermal, mechanical and optical properties.[1] It is the only stable binary phase in the Al_2O_3–SiO_2 system.[2,3] As a matter of fact, pure mullite is a solid solution with composition $Al_2[Al_{2+2x}Si_{2-2x}]O_{10-x}$, being $0.17 \le x \le 0.5$.[4,5] It is assumed that stable mullites exist in the range of compositions between $3Al_2O_3{\cdot}2SiO_2$ and $2Al_2O_3{\cdot}SiO_2$, herewith referred as 3:2 and 2:1, respectively. Recent studies of mullite synthesis have emphasized the utilization of chemically synthesized precursors which convert into mullite in a low temperature range from ~850 to ~1250 °C.[6–10] According to the homogeneity of prepared gels two categories of preparation routes can be considered. First, single-phase or molecularly mixed gels, in which aluminium and silicon species exhibit homogeneity on the molecular level, crystallize directly a metastable alumina-rich mullite with $x > 0.40$ at ~980 °C.[11] In the other type of gels, colloidal or diphasic gels, in which the scale of homogeneity is in the range from 10 to 100 nm, mullite crystallizes at ~1250 °C via spinel formation at ~980 °C.[12]

The influence of several additives, such as Ti, Zr, Mg, etc., on the temperature and formation rate of mullite during the process of mullitization of kaolinite has been studied[13–15]. Also, there are some available reports regarding with the effect of various impurities on mullite formation in diphasic gels.[16–18] However, there is very few information dealing with the role played by these impurities in the mullitization of monophasic gels. Okada and Osuka cited their unpublished study of the effects of Li, Na, K, Mg, Ca, Ti and Zr on gels prepared by both slow and rapid hydrolysis, in which they conclude that these cations act as inhibitors in mullite formation.[19] Recently, Nass et al. reported results on the incorporation of several amounts of chromium into the monophasic gels and their influence on the mechanism of mullite formation.[20]

Titanium oxide is often used as nucleating agent for crystallization of different crystalline phases on controlled heating gels precursors.[21,22] As a matter of fact the action of Ti^{+4} cation has allowed the controlled crystallization of desirable phases in some glasses heated at low temperature.[23,24] Some results on the

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doi:10.1016/j.jeurceramsoc.2006.09.014

solubility of titanium oxide in 3:2 mullite synthesized by conventional laboratory techniques have already been reported but data on the role played by the titanium oxide during the reaction sequence at low temperature in 3:2 mullite monophasic gels are still scanty.[25–29] Thus, it seems to be interesting a systematic study concerning the mullitization of titanium-containing 3:2 mullite monophasic gels. Likewise, it would be also valuable to extend the study to 2:1 mullite single-phase gels, in order to compare thermal behaviours of either end-member of mullite gels.

In the present paper, therefore, the preparation and reaction sequence at low temperature of TiO_2-containing 3:2 and 2:1 mullite gel precursors were investigated and results regarding the crystallization kinetics, phases developed and microstructural characterization were reported. The effect of TiO_2 on the structural and microstructural evolution of both binary gels was studied for progressive addition of titanium oxide to the batches of the undoped binary gels.

2. Experimental procedure

2.1. Preparation of gels

Monophasic TiO_2-containing mullite gels with increasing amounts of titanium were synthesized by the semialkoxide method. Two series of mullite gels were prepared with $(Al_2O_3 + TiO_2)/(SiO_2)$ molar ratios 3/2 and 2/1. The chemical formula of both series can be write out as $3(Al_{2-x}Ti_xO_3)\cdot 2(SiO_2)$ and $2(Al_{2-x}Ti_xO_3)\cdot(SiO_2)$, with $x = 0$, 0.02, 0.05, 0.07, 0.10 and 0.15. The composition and nomenclature of both series of gels are displayed in Table 1. Ten grams of final pure and TiO_2-doped mullite samples of both series were synthesised. Gels were prepared by the following procedure. A solution of aluminium nitrate nonahydrate was obtained by refluxing $Al(NO_3)\cdot 9H_2O$ in absolute ethanol for 2 h. Then a solution of tetraethylorthosilicate (TEOS), Fluka >98%, in absolute ethanol was added. The resulting solution was refluxed for 6 days. After that time, the titanium isopropoxide (TiP), Merck, was added to the above resulting solution and the mixture refluxed again for 2 days. The final solutions were translucent in all cases and after aging in a beaker covered with a holed plastic for 4 weeks gels were obtained. The gels were dried at 110 °C for 24 h and thermal treated at the heating rate of 30 °C/min to temperatures between 900 and 1100 °C and annealed for 2 h.

Table 1
Compositions of synthesized titanium-containing 3:2 and 2:1 mullite gels

Gel	SiO_2	Al_2O_3	TiO_2
3:2	40.00 (28.15)[a]	60.00 (71.85)	–
32t02	39.77 (26.92)	59.04 (71.98)	1.19 (1.10)
32t05	39.41 (26.77)	57.64 (69.51)	2.95 (2.73)
32t07	39.18 (26.67)	56.71 (69.51)	4.11 (3.82)
32t10	38.83 (26.51)	55.34 (68.05)	5.83 (5.43)
32t15	38.25 (26.26)	53.13 (65.67)	8.62 (8.07)
2:1	33.33 (22.65)	66.66 (77.35)	–
21t02	33.08 (21.63)	65.59 (77.19)	1.33 (1.18)
21t05	32.77 (21.51)	63.96 (75.56)	3.27 (2.93)
21t07	35.59 (21.44)	62.85 (74.47)	4.56 (4.09)
21t10	32.23 (21.29)	61.31 (72.90)	6.46 (5.81)
21t15	31.75 (21.10)	58.73 (70.27)	9.52 (8.63)

[a] wt% in brackets.

2.2. Techniques of characterization

In order to follow the chemical and structural transformations of gels through the thermal treatment, the following techniques were used.

Differential thermal analysis (Model Pyris Diamond TG/DTA, Perkin Elmer, Norwalk, Connecticut, U.S.A.) was carried out in nitrogen with Pt liners, using a heating rate of 10 °C min^{-1}.

Magic angle spinning nuclear magnetic resonance (Model Unity300, Varian, San Francisco, USA) was done on a spectrometer operating at 78.1 MHz for ^{27}Al. The spinning rate was 5 kHz. A delay time of 5 s and a radio-frequency pulse of 4 μs were used. $Al(H_2O)_6{}^{+3}$ was used as external standard reference.

X-ray diffraction analysis (Model D-500, Siemens, Karlsruhe, Germany) was performed using a graphite monochromatic Cu Kα radiation operating at 30 kV and 40 mA. X-ray diffraction patterns were run between 15° and 90° ($2\theta°$) range, with a step size of 0.02° ($2\theta°$) and a counting time of 10 s. CaF_2 was used as external standard. Lattice parameters were calculated by a least squares fit.

The microstructure of the as-prepared and thermally treated samples was observed by field emission scanning electron microscopy (Model S-4100, Hitachi Ltd., Tokyo, Japan) working at 30 kV. To improve the quality of the observation, the samples were etched with a HF solution for different times, and subsequently washed with H_2O. The morphology of dried gels and mullite particles was also examined using transmission electron microscope (Model JEM-1010, Jeol Ltd., Tokyo, Japan) at an accelerating voltage of 100 kV. Samples were prepared by dispersing HF etched calcined powders in absolute ethanol and setting drop-wise on copper grids that had previously been coated with a holey thin carbon film.

3. Results and discussion

3.1. Differential thermal analysis of gels

DTA curves for titanium oxide-doped 3:2 and 2:1 mullite gels are displayed in Figs. 1 and 2. The exothermic effect corresponding to the crystallisation of both pure nominal 3:2 and 2:1 mullite appears at around 980 °C as reported previously.[30] In both TiO_2-doped 3:2 and 2:1 mullite series a decrease in the crystallization temperature is observed on increasing the amount of TiO_2, as shown in the above Figs. 1 and 2. In general, the broad exothermic peak is the resultant of two distinct peaks, as can be clearly distinguished in some of the DTA traces. In principle, each exothermic DTA effect is associated to a crystallization process. The first point to be elucidated, therefore, will be to check if both peaks are associated to the same or different crystallization process. The way is to stop DTA runs of gels after the thermal effect and analyze by X-ray powder diffraction the cooled specimen. XRD patterns of both series of samples are displayed

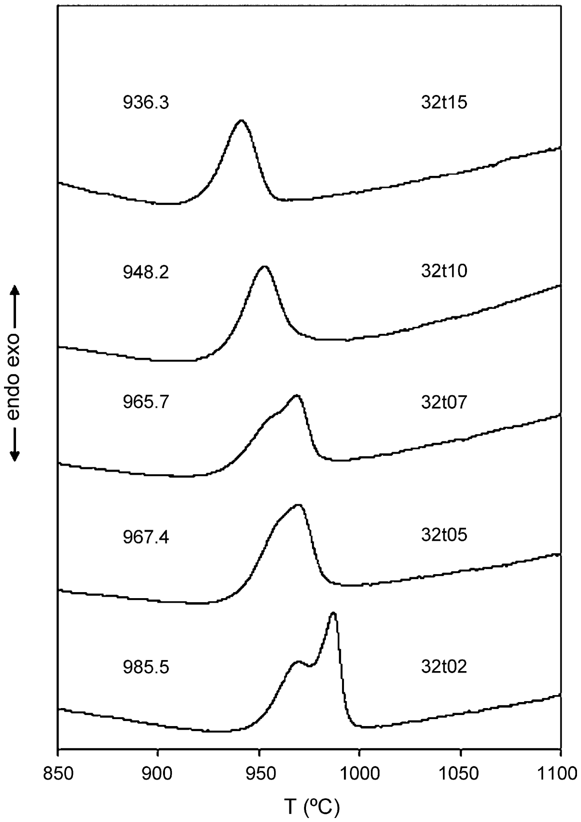

Fig. 1. DTA curves of TiO_2-containing 3:2 mullite gel series performed at 10 °C min^{-1} in nitrogen.

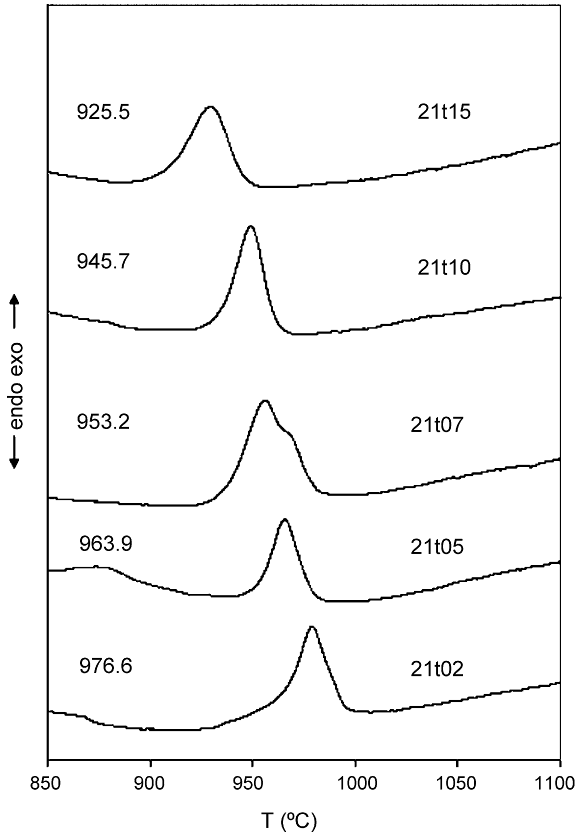

Fig. 2. DTA curves of TiO_2-containing 2:1 mullite gel series performed at 10 °C min^{-1} in nitrogen.

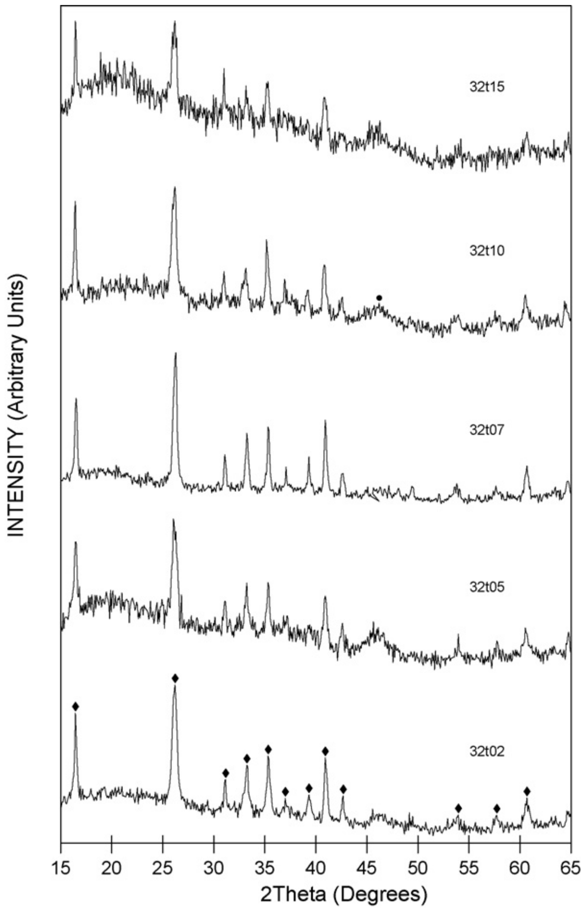

Fig. 3. XRD patterns of TiO_2-doped 3:2 gel series cooled at the end temperatures of the broad exothermic effects (◆ is mullite and ● is alumina-silica spinel).

in Figs. 3 and 4. All samples displayed mullite as main crystalline phase as well as a small amount of alumina-silica spinel. Pask and Tomsia reported that colloidal gels formed from single-phase gels did not nucleate mullite but formed an Al–Si spinel that not cause the formation of an exothermic peak at 980 °C in a DTA experiment.[6] Therefore, coupled results from XRD and DTA suggest the crystallization of two phases with mullite structure. It is also to be noted that the intensity of mullite peaks lowers when the nominal titanium oxide content (x) in gels is higher than 0.07.

As previously reported the strong DTA peak in the pure 3:2 gel was associated to mullite formation but it was also noted that even under fast heating some phase separation occurred.[30] As a consequence two mullites formed at low temperature: one SiO_2-richer and the other Al_2O_3-richer. Likewise, for TiO_2-containing gels the two-component broad peaks in the DTA traces can also be attributed to the crystallization of two mullite phases, both incorporating Ti^{+4} into the mullite structure; one silica-rich mullite and other richer in alumina. For the titanium-doped 2:1 gel series the broad exothermic effect is also caused by the crystallization of Al_2O_3-rich and SiO_2-rich mullites. From these results it is evident that the addition of titanium oxide to gels favours the direct formation of mullite. This behaviour may be explained by assuming that a relatively high degree of chemical homogeneity is attained in the gel. In this sense, it seems that the

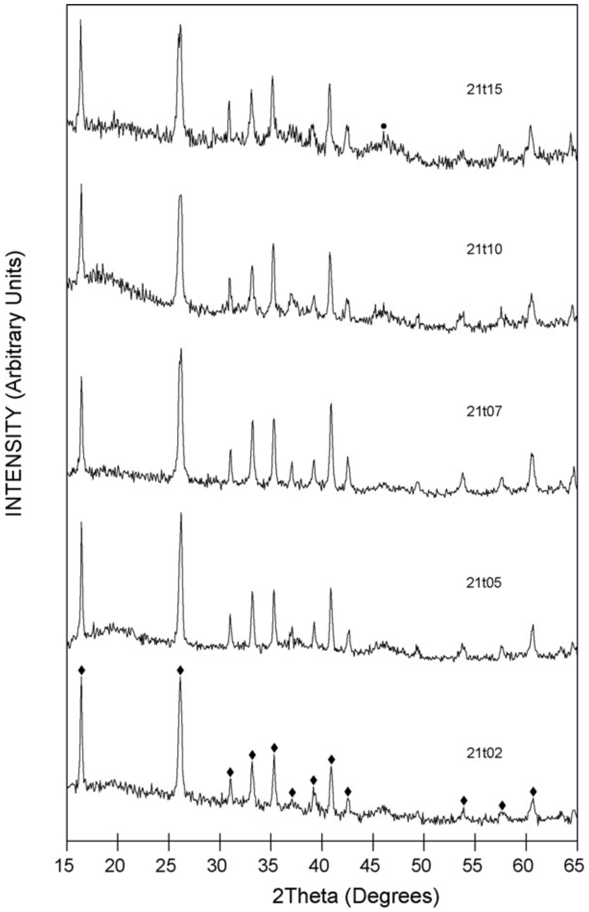

Fig. 4. XRD patterns of TiO_2-doped 2:1 gel series cooled at the end temperatures of the broad exothermic effects (◆ is mullite and ● is alumina-silica spinel).

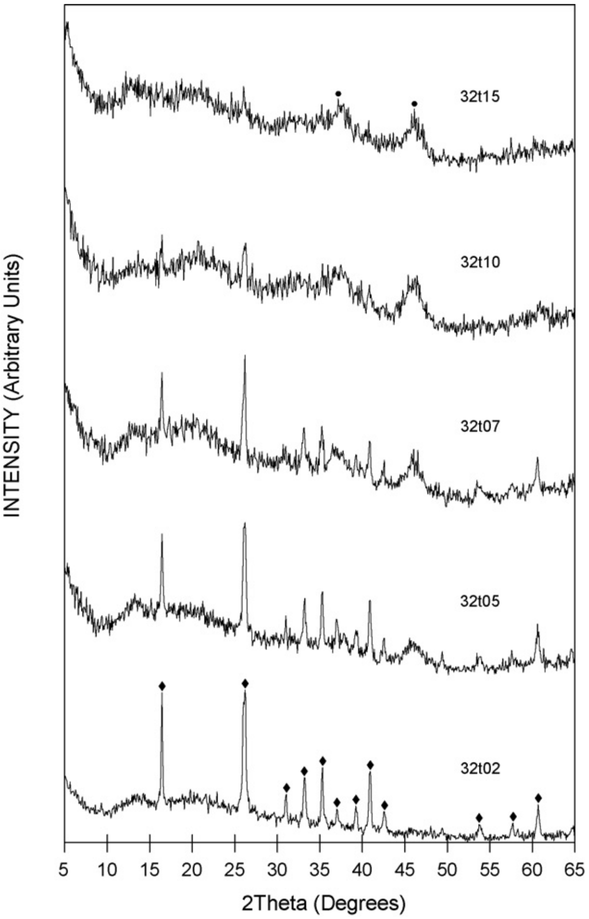

Fig. 5. XRD patterns of TiO_2-doped 3:2 gels thermally treated at 900 °C for 2 h (◆ is mullite and ● is alumina-silica spinel).

role of titanium in the gel transformation, at least up to certain contents, is not to promote an extended phase separation which would give rise to the crystallization of titanium-containing alumina-silica spinel but to favour the mullite formation by its uniform distribution in the gel. In fact, this kind of crystallization path is followed by pure mullite precursors, in which a high chemical homogeneity is reached in the chemical synthesis and maintained during the thermal processing of gel precursors.[30]

3.2. Formation of mullite from gels

In order to minimize the potential phase separation associated with the heating schedule used in the thermal treatment of TiO_2-doped mullite gels, two relatively fast schedules have been used. In the first one, gels were heated with a heating rate of 30 °C/min and holding the specimen 2 h at the final temperature. At 800 °C very small XRD peaks associated with the formation of mullite are detected in all gels except in those with the higher amount of titanium ($x = 0.10$ and 0.15), which remain amorphous. Fig. 5 display the evolution of doped 3:2 gels series with increasing doping level, from $x = 0.02$ to 0.15, on heating at 900 °C. The evolution is very similar for the series 2:1. In both series, gels with the higher titanium content, which were amorphous at 800 °C, display spinel as single crystalline phase. The rest of gels containing amounts of titanium up to $x = 0.07$, show more intense mullite peaks as well as new, weak peaks associated to spinel. At 1000 °C the intensity of the mullite peaks in the heated gels increases independently of their titanium oxide content. Finally, at 1100 °C very strong peaks of orthorhombic mullite are present in XRD patterns of both series of gels. In general, the thermal evolution of titanium oxide-doped 2:1 gels is similar to the one followed by 3:2 gels.

The evolution of gels with the above thermal schedule is similar to the one showed under a second almost isothermal heating, i.e. a heating rate of 40 °C min^{-1} and no holding time at the final temperature. XRD patterns of gels of the 3:2 series submitted to the above fast heating (not showed) are very similar to the ones heated under the relatively slower schedule and additional holding at the final temperature for 2 h. Therefore, we can assume that the spinel formation in the processing of these monophasic gels is not due to a relatively slow thermal processing but it is a characteristic of these TiO_2-containing single-phase gels. Similar results have been reported by Nass et al. for single-phase mullite gels doped with chromium.[20] They claimed that under non-isothermal treatment, i.e. with slow heating rate, a two-step phase separation can be proposed: the first step was the separation into alumina-rich and silica-rich phase; and the second one was clustering of the alumina-rich phase. Under isothermal heat treatment, i.e. fast heating rates, they found that the second-step phase separation could be completely suppressed and, therefore, Cr-doped mullite was the only crystalline phase in the whole range of temperature. The thermal treatment used in our study is not as fast as the one used by Nass et al.[20] in which samples were rapidly inserted into a tube furnace held at maximum temperature an annealed for 2 h, but it can be considered a relatively fast heat treatment as previously demonstrated for pure mullites.[30]

The role played by titanium in the titanium oxide-doped monophasic mullite gels is, therefore, believed to be primarily a result of the microphase separation process occurred in alumina-silica gels. From two TiO_2-containing separated areas, one richer in alumina and the second more rich in silica, two phases crystallise almost simultaneously displaying mullite structure. The phase separation leading to the crystallization of spinel is favoured by both, a high amount of TiO_2 or a decrease of the heating rate. The homogeneous distribution of titanium in both separated areas can be explained by the ability of titanium to be incorporated into the Al_2O_3–SiO_2 amorphous matrix, as reported Sugai and Somiya for glasses in the system SiO_2–TiO_2–Al_2O_3.[31]

From the above results it can be draw that additions of titanium oxide, in the range 4–4.5 wt%, to binary 3:2 and 2:1 Al_2O_3–SiO_2 gels favour the formation of mullite at lower temperatures when gels are heated at a relatively high heating rate.

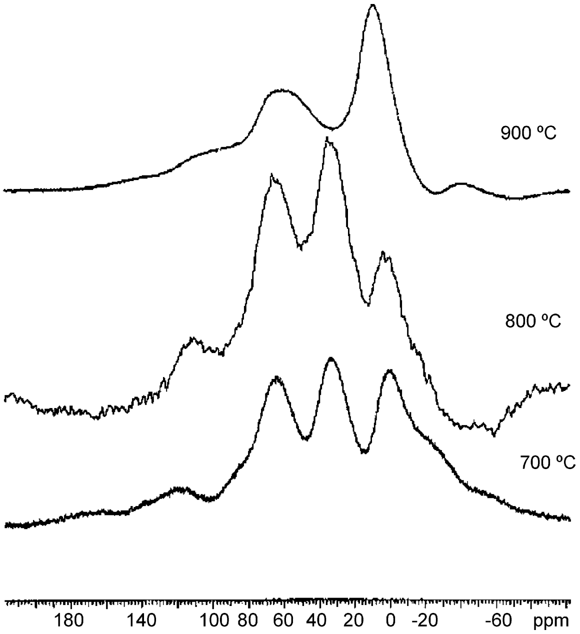

Fig. 7. ^{27}Al NMR spectra of 21t05 gels heated at several temperatures.

3.3. Structural changes from gels to mullite

In order to evidence the local structural changes in the transformation from gel to mullite, the heated gels 3:2 and 2:1 with increasing titanium oxide contents were analysed by ^{27}Al NMR spectroscopy. In Figs. 6 and 7 are shown the ^{27}Al NMR spectra of titanium-containing 3:2 and 2:1 gels ($x = 0.05$) heated at temperatures from 700 to 900 °C, respectively. The above spectra display peaks at around 65, 34 and 0 ppm. Three types of environments: four-, five- and six-coordinated aluminium sites have been reported in amorphous aluminosilicate and glassy materials, which are generally located in the range 50–80, 30–40 and −10 to +15 ppm, respectively.[32,33] As it was previously reported the environment of the aluminium in dried gels is predominantly hexa-coordinated.[30] However, at as low temperature as 500 °C the ^{27}Al NMR spectra of samples indicate the occurrence of aluminium in the three geometrical surroundings. On heating at relatively high temperature, i.e. 900 °C, the peak associated to the five-coordinated aluminium disappears and only tetrahedral and octahedral coordinated aluminium are detected. The aluminium distribution in both mullite types at 900 °C seems to be irrespective of the doping amount as shown in Figs. 8 and 9. From the above figures, both six-coordinated and tetra-coordinated environments are detected in both heated titanium oxide-containing mullite gel series. The obtained results indicate that the evolution experienced by the coordination of

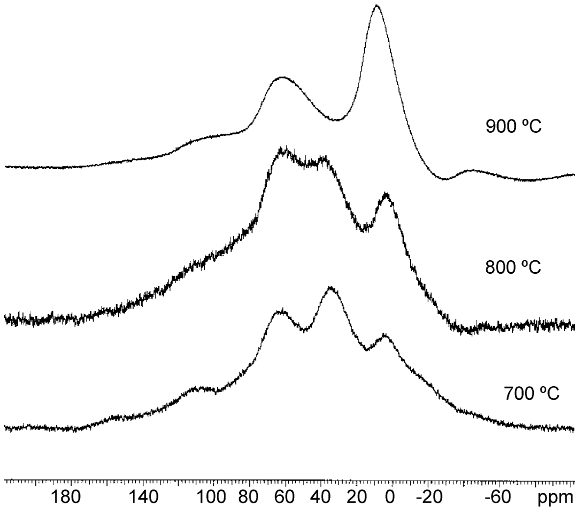

Fig. 6. ^{27}Al NMR spectra of 32t05 gels heated at several temperatures.

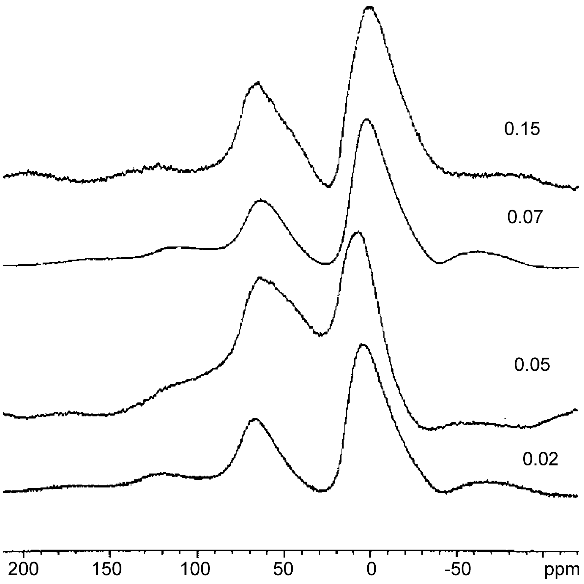

Fig. 8. ^{27}Al NMR spectra of 3:2 gel series heated at 900 °C for 2 h.

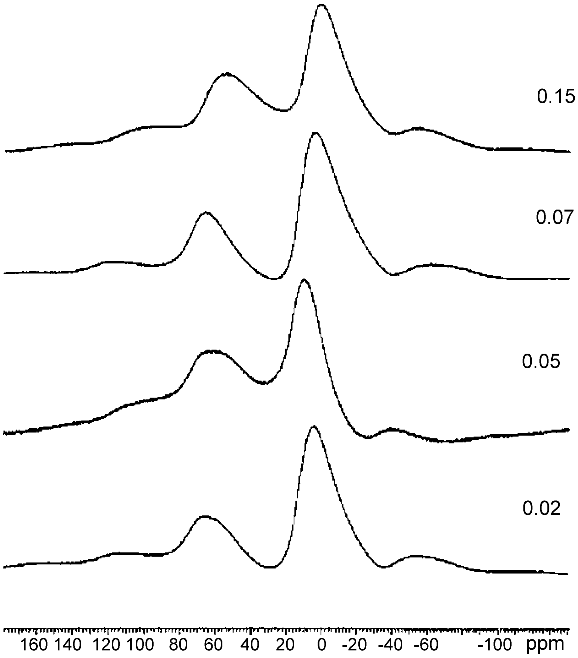

Fig. 9. ^{27}Al NMR spectra of 2:1 gel series heated at 900 °C for 2 h.

aluminium cation in titanium-doped mullite gels is very similar to the ones detected in pure mullites.

3.4. Lattice parameters of titanium-doped mullites heated at 1100 °C

The lattice parameters for pure and titanium oxide-doped mullites 3:2 and 2:1 thermal treated at 1100 °C for 2 h are shown in Tables 2 and 3. The corresponding lattice volume variation for both series of mullites is displayed in Fig. 10. As can be seen, in general, the parameter *a* for pure mullites at 1100 °C are lower than the ones displayed at 900 °C. These results are in agreement with the general trend observed in heated pure mullite gels, since on increasing the final temperature from 900 to 1100 °C mullites become SiO_2-richer.[11] In respect of changes experienced by both series of TiO_2-containing 3:2 and 2:1 mullite gels with increasing the amount of doping, it is to be noted that a continuous increase of the unit cell volume occurred. The increase in the lattice volume is greater in the series of 2:1 than in 3:2. These results are consistent with the raise of Ti^{+4} cation incorporated into the mullite structure as the nominal amount of TiO_2 increases in both gel series. The results in the above Tables indicate that almost there are no changes in the lattice parameter *a* while both the parameters *b* and *c* are greater and greater on increasing the starting nominal TiO_2. It is well known a certain preference of the Ti^{+4} cation to entry in octahedral surroundings.[34] However, titanates and other titanium-doped silicate phases have also been reported in which the tetravalent titanium occupies tetrahedral sites.[21]

The large increase of both lattice parameters b and c, and as consequence the lattice volume, in both series of TiO_2-doped mullites on increasing the nominal amount of TiO_2, can be understood assuming one of the two possible mechanisms of substitution: by the first one, the Al^{+3} is replaced by Ti^{+4} and, to balance the charge, the Si^{+4} is replaced by Al^{+3}, as previously suggested by Schneider.[26] Both simultaneous processes will bring a net increase in the lattice parameters. The other possible mechanism is the direct replacement of Si^{+4} by Ti^{+4}. In this case, it will be produced an increase in the lattice dimensions too. From the large variation of lattice parameters can be suggested that the main mechanism in the solid solution formation is the location of Ti^{+4} in octahedral sites substituting to Al^{+3} coupled with the substitution of Si^{+4} by Al^{+3} in tetrahedral sites, which is required for excess charge compensation.

Table 2
Lattice parameters of titanium-doped gel 3:2 thermal treated at 1100 °C for 2 h under heating rate of 30 °C/min

	a (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)
3:2[a]	7.5746 (4)	7.6963 (4)	2.8788 (2)	167.87 (1)
3:2	7.5740 (3)	7.6882 (3)	2.8812 (2)	167.77 (1)
32t02	7.5683 (2)	7.6908 (2)	2.8860 (2)	167.98 (1)
32t05	7.5714 (3)	7.6961 (2)	2.8893 (2)	168.36 (1)
32t07	7.5723 (3)	7.6974 (3)	2.8909 (2)	168.50 (1)
32t10	7.5759 (3)	7.7025 (3)	2.8932 (2)	168.83 (1)
32t15	7.5732 (3)	7.7054 (3)	2.8967 (2)	169.04 (1)

[a] Heated at 900 °C.

Table 3
Lattice parameters of titanium-doped gel 2:1 thermal treated at 1100 °C for 2 h under heating rate of 30 °C/min

	a (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)
2:1[a]	7.5910 (4)	7.6893 (4)	2.8836 (3)	168.32 (1)
2:1	7.5828 (3)	7.6832 (3)	2.8841 (3)	168.03 (1)
21t02	7.5689 (2)	7.6883 (2)	2.8879 (4)	168.05 (1)
21t05	7.5778 (2)	7.6927 (2)	2.8917 (2)	168.57 (1)
21t07	7.5800 (2)	7.6967 (2)	2.8925 (3)	168.75 (1)
21t10	7.5894 (2)	7.7036 (2)	2.8973 (4)	169.39 (1)
21t15	7.5883 (2)	7.7112 (2)	2.9018 (2)	169.80 (1)

[a] Heated at 900 °C.

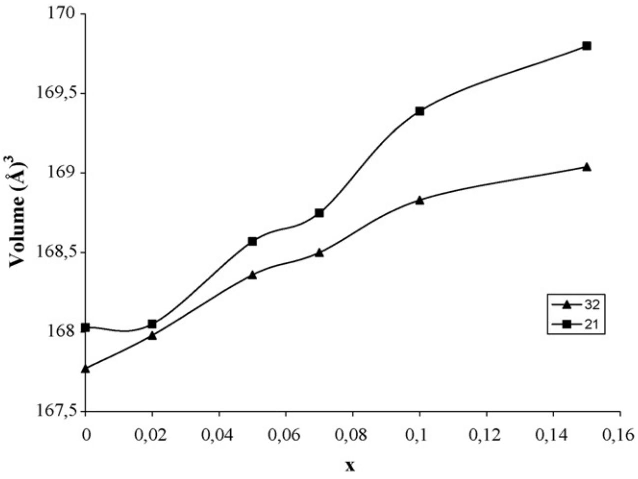

Fig. 10. Volume cell of 3:2 and 2:1 gel series heated at 1100 °C for 2 h.

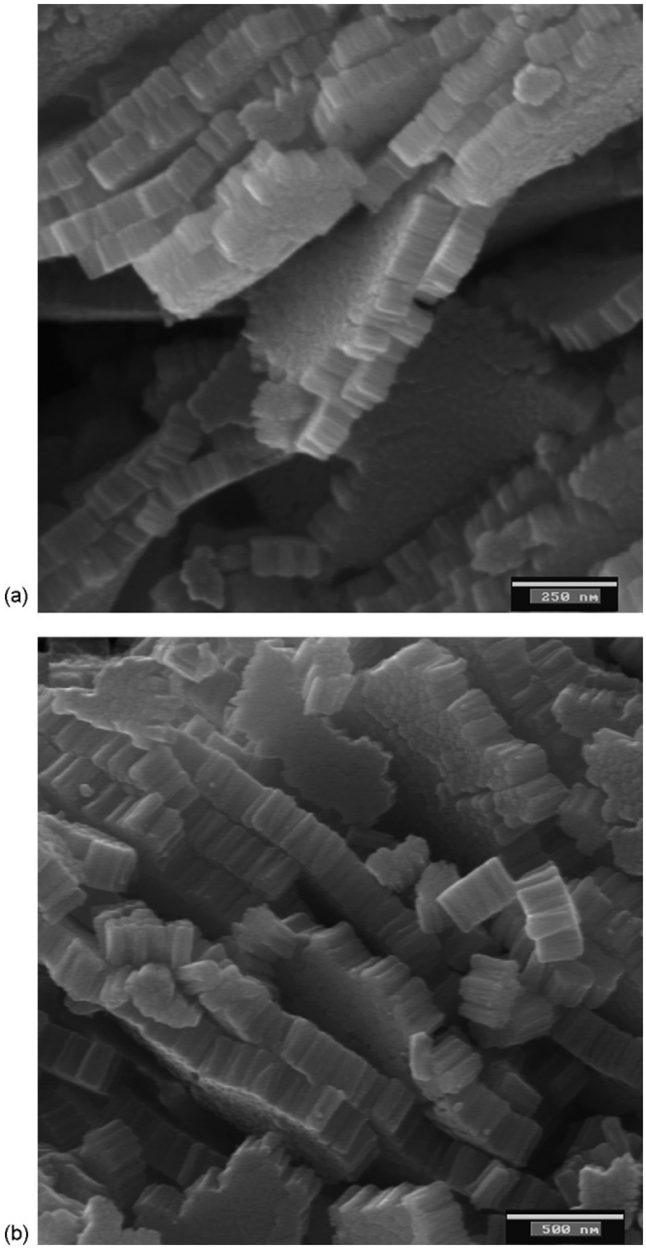

Fig. 11. FESEM of TiO_2-containing 3:2 mullite gels thermal treated at 1100 °C for 2 h: (a) 32t07; (b) 32t15.

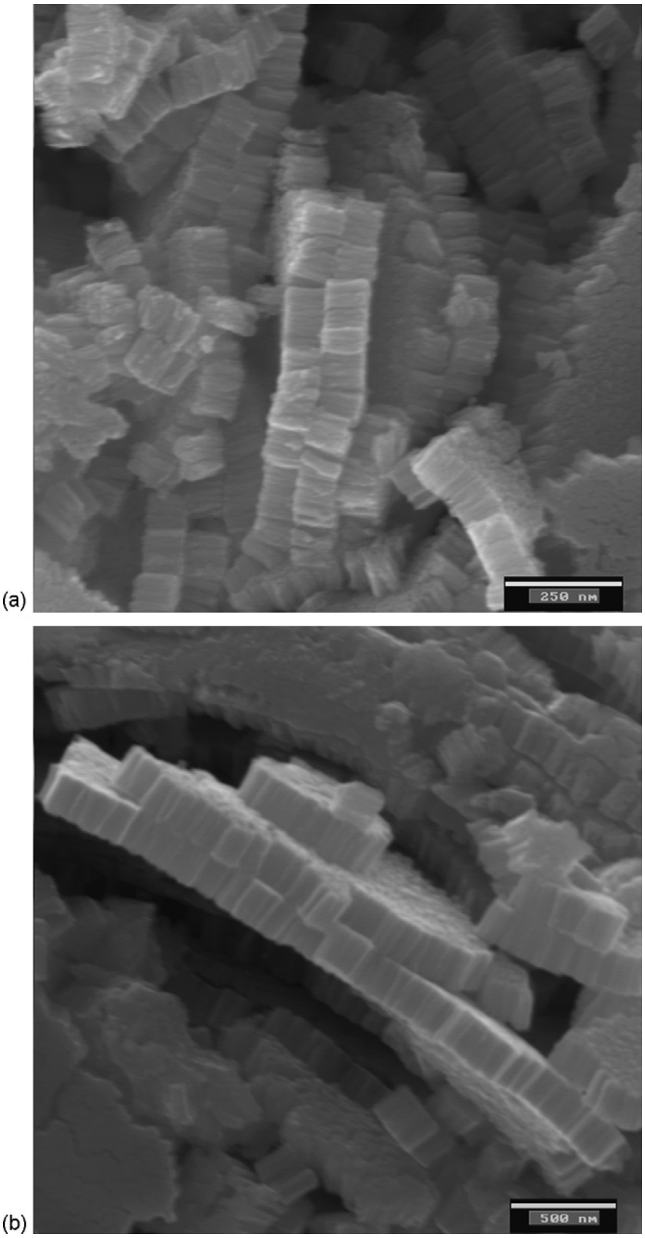

Fig. 12. FESEM of TiO_2-containing 2:1 mullite gels thermal treated at 1100 °C for 2 h: (a) 21t07; (b) 21t15.

3.5. Microstructural evolution from gels up to mullites prepared at 1100 °C

In both types of gels heated at 900 °C, in which mullite is already formed, the nanocrystals of mullite are immersed in the residual glassy phase. We refer mullite crystals as nanocrystals according with the fact that at least one dimension is smaller than 100 nm. In this respect, it is to be noted that even when the amount of residual glassy phase is quite low, is very difficult to remove it without partially dissolving mullite nanocrystals. On increasing the temperature, nanocrystals grow slightly and at 1100 °C an extended arrangement of well-formed TiO_2-containing mullite nanocrystals is clearly formed. This feature can be seen in Figs. 11 and 12 corresponding to gels 32t07, 32t15, 21t07 and 21t15 after thermal treatment at 1100 °C. This kind of arrangement was previously observed for pure 3:2 and 2:1 gels heated at 1200 °C.[35] However, the size of mullite nanocrystals increases with raising the amount of titanium oxide. From Figs. 11 and 12, it can also be appreciated that the size of nanocrystals for both types of mullites 3:2 and 2:1 with a relatively low titanium amount, i.e. $x = 0.07$, is around 70 nm large and 30 wide, while the nanocrystals with the higher titanium amount ($x = 0.15$) are almost twice, i.e. in the limit size for their consideration as nanocrystals. A representative TEM image of mullite nanocrystals formed in the doped 32t07 and 21t07 gels at 1100 °C are shown in Fig. 13(a) and (b), respectively. From them the presence of nanocrystals is confirmed.

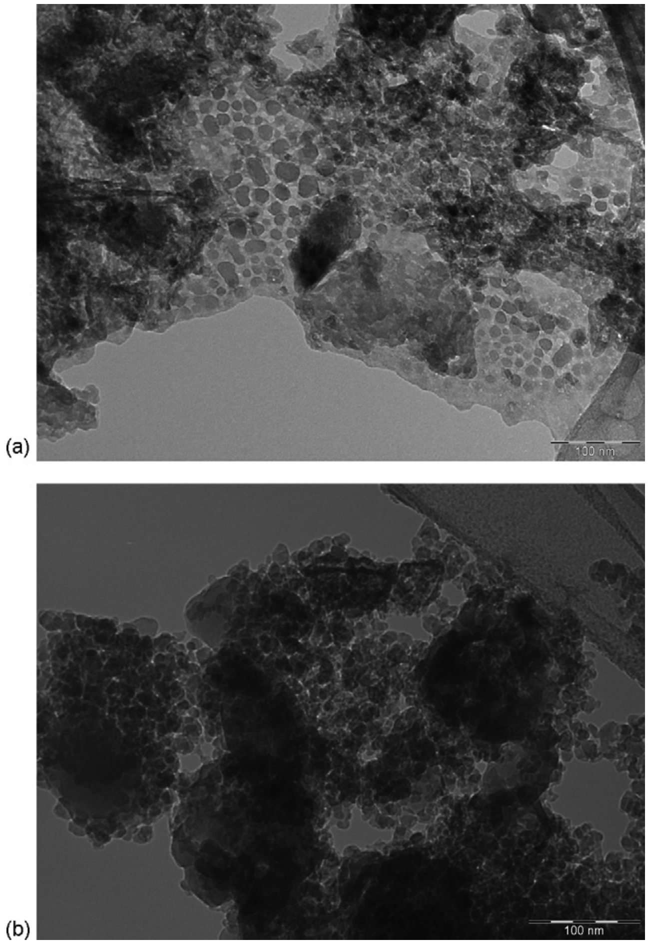

Fig. 13. TEM of mullite nanocrystals formed in doped gels at 1100 °C for 2 h: (a) 32t07; (b) 21t07.

As in the pure mullite gels, the almost mono-sized, regular arrangement of mullite nanocrystals arisen from the TiO_2-doped mullite gels suggests again that nucleation of mullite crystals is the kinetics controlling step in the mullite formation process. Thus, the crystal growth step is relatively fast.

4. Conclusions

Single-phase gels with compositions $3(Al_{2-x}Ti_xO_3)\cdot 2(SiO_2)$ and $2(Al_{2-x}Ti_xO_3)\cdot(SiO_2)$, with $x = 0, 0.02, 0.05, 0.07, 0.10$ and 0.15, were prepared by gelling mixtures of aluminium nitrate, tetraethylorthosilicate and titanium isopropoxide. Chemically homogeneneous gels were synthesized and transformed to mullite at low temperature. ^{27}Al NMR spectra showed the evolution of penta-coordinated aluminium to hexa-coordinated and tetra-coordinated when mullite crystallized. DTA and XRD results confirmed the shifting of the mullite formation to lower temperatures for both TiO_2-containing 3:2 and 2:1 monophasic gels. The lattice parameter trend of mullite single-phase gels heated at 1100 °C on increasing the amount of nominal TiO_2 in gel precursors indicated that the amount of TiO_2 incorporated into solid solution raised in both series. FESEM and TEM images of heated gels at 1100 °C displayed the formation of well-shaped parallelepiped of mullite nanocrystals with crystal anisotropy.

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