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Solubility and microstructural development of TiO_2-containing $3Al_2O_3{\cdot}2SiO_2$ and $2Al_2O_3{\cdot}SiO_2$ mullites obtained from single-phase gels

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Abstract

The interdependence of the titanium oxide amount and the anisotropic growth of mullites prepared from single-phase gels were investigated. Gels with stoichiometries $3(Al_{2-x}Ti_xO_3){\cdot}2(SiO_2)$ and $2(Al_{2-x}Ti_xO_3){\cdot}(SiO_2)$, with $0 \le x \le 0.15$ were prepared by the semialkoxide method. Gels and specimens heated at temperatures between 1200 and 1600 °C were characterized by using infrared spectroscopy (IR), X-ray diffraction (XRD) and transmission and field emission scanning electron microscopies (TEM and FESEM). Al_2TiO_5 as minor impurity was detected in both series of mullites for gel precursor compositions $x = 0.10$ and $x = 0.15$, obtained at temperatures between 1200 and 1600 °C. Variations of lattice parameters of mullite, processed at temperatures from the range between 1400 and 1600 °C, with the starting nominal amount of titanium oxide indicated that the solubility limit of titanium oxide was in ranges 3.8–4.1 and 4.1–4.4 wt% TiO_2 for 3:2 and 2:1 mullites series, respectively. The anisotropic growth of titanium-doped mullite crystalline grains was significant only when the nominal amount of titanium oxide exceeded the limit of solubility into the mullite structure (for both mullite series). Stronger anisotropy occurred for the 3:2 series specimens, i.e. for the SiO_2-richer mullites. In both series of mullites, the anisotropic grain growth was observed for the process temperatures higher than 1400 °C; the crystalline grains of mullites processed at lower temperatures were equiaxials and of almost the same size.

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

1. Introduction

Mullite-based materials are important for their thermal, mechanical and optical properties.[1] Consequently, they are used in a great number of applications. The mullite structure can be described as edges-shared AlO_6 octahedron chains parallel to *c*-axis bounded by aluminium and/or silicon tetrahedra.[2] The pure mullite phase, which is the only binary compound in the Al_2O_3–SiO_2 system, is a solid solution whose composition may be written as $Al_2[Al_{2+2x}Si_{2-2x}]O_{10-x}$, being $0.18 \le x \le 0.82$.[3] The stable end-members of that solid solution have compositions $3Al_2O_3{\cdot}2SiO_2$ ($x = 0.25$) and $2Al_2O_3{\cdot}SiO_2$ ($x = 0.40$), hereafter referred to as 3:2 and 2:1, respectively. Mullite-based solid solutions are interesting because their properties can be modulated as a function of the dopant amount.[4] A number of mullite solid solutions have been described in the literature.[5–9] Titanium-containing mullite solid solutions have been previously reported by several authors.[10–14] In general, it is to be noted that all published data concerning TiO_2 solubility in mullites are referred to the silica-richer mullite, 3:2. Murthy and Hummel reported a study of the solid solution of TiO_2 in 3:2 mullite by measuring the changes in lattice parameters and unit-cell volume.[10] The approximate minimum temperature required for the formation

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of solid solution from mixtures of synthetic mullite and titanium oxide was 1400 °C; the maximum amount of TiO_2 in solid solution was estimated in range 2–4 wt%. Green and White studied the solid solubility limits of the mullite phase in the ternary system Al_2O_3–TiO_2–SiO_2. Schneider claimed that the maximum amount of Ti^{4+} cation incorporated into mullite was ∼4.2 wt% TiO_2 but as far as we know no detailed experimental results have been reported.[12] Hong and Messing reported on the transformation kinetics, densification and anisotropic grain growth in diphasic-gel-derived titania-doped mullite.[13,14] Most of the studies on TiO_2-doped mullites were carry out for specimens produced from oxide powder mixtures or colloidal gel precursors under air furnace atmosphere. Recently, some attempts at studying the reaction sequence of Ti^{4+}- and M^{2+}-codoped mullites from gels have been reported. Sales et al. in a study on mullitization of coupled Ti^{4+}- and Ni^{2+} or Co^{2+}-containing 3:2 mullite gels found the formation of solid solutions containing both cations.[15–18] Moreover, the results indicated the formation of nickel or cobalt aluminate spinel-mullite composites which could be used as ceramic pigments at high temperatures.

It is well known that sol–gel techniques allow the preparation of monophasic precursor gels leading to metastable and stable phases at softer conditions. By preserving the high chemical homogeneity of those gels during the thermal treatment is possible to favour the formation kinetics of a final desired crystalline phase and even to increase the solubility of some doping cation into the host lattice. The preparation of single-phase mullite gels enabling formation of mullite crystalline phase at around 1000 °C has been extensively studied.[19–24] In order to the direct and solely formation of mullite it is required to maintain the chemical homogeneity of the precursor during the chemical synthesis of gels and during the thermal processing.[25,26]

An additional interest to study titanium oxide-doped mullites from single-phase gels is the possibility of developing doped mullite materials with interpenetrating anisotropic grain growth. These doped mullite-based materials could have improved mechanical properties.

In the present paper, therefore, we will report the formation and characterization of TiO_2-doped 3:2 mullite solid solutions obtained from single-phase gel precursors. Furthermore, we intend to extend this study to 2:1 mullites and to check whether the solubility of TiO_2 in mullite depended on its composition. Finally, it is also our target to examine whether anisotropic grain growth occurred in TiO_2-doped mullites prepared from single-phase gels and its possible dependence on the extension of doping, composition of mullite and temperature of the thermal treatment.

2. Experimental procedure

2.1. Preparation of samples

Gels with increasing amounts of titanium, with stoichiometries $3(Al_{2-x}Ti_xO_3)\cdot 2(SiO_2)$ 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 synthesized. Hereafter the specimens will be referred to as 32t00 and 21t00 for the undoped and 32t02, 32t05, 32t07, 32t10 and 32t15 for the 3:2 mullites with increased loads of TiO_2. Likewise, the specimens in the TiO_2-doped 2:1 mullite series will be similarly labelled from 21t02 to 21t15. 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. To the aluminium solution a solution of tetraethylorthosilicate (TEOS), Fluka >98%, in absolute ethanol was added and 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 was refluxed again for 2 days. The final resulting solutions were translucent in all cases; gels were obtained by aging them in a beaker covered with a holed plastic foil for 4 weeks. The gels were dried at 110 °C for 24 h and thermally treated by heating with rate of 30 °C/min to temperatures between 900 and 1600 °C and annealing for 2 h.

2.2. Characterization techniques

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

X-ray diffraction analysis (Model D-500, Siemens, Karlsruhe, Germany) was performed using a graphite monochromatic Cu Kα radiation. Lattice parameters were determined by using CaF_2 as external standard from XRD patterns registered for diffraction angles 2θ of 15–70° with 0.02° scan step and fixed exposure time of 10 s. A least squares fit was used to calculate the lattice parameters.

Infrared absorption spectra (Nicolet-Avatar, Perkin-Elmer Ltd., Beaconsfield, Buckinghamshire, England) were obtained in the range 1400–400 cm^{-1} using the KBr pellet method.

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 20–30 kV. To check the quality of the observation, some of the samples were etched with a diluted HF solution for 10 s, and subsequently washed with H_2O.

Energy-dispersive X-ray analysis was performed using a scanning electron microscope (Model JSM-6300, Jeol, Oxford, England) operated at 20 kV. This instrument is equipped with an energy dispersive X-ray spectrometer (Pentafet, Oxford Instruments, Knoxwille, TN). Specimens were mounted in a polymer resin and polished with progressively finer SiC papers. Samples were carbon coated before acquiring the X-ray spectra.

3. Results and discussion

3.1. Formation and lattice parameter variations of solid solutions

The crystalline phases detected after heating gels containing small amounts of titania, at as low temperature as 900 °C, are mullite and alumina-silica spinel. In general, the XRD peaks associated to the spinel phase were very weak except for specimens from both gels with the largest nominal amount of titanium

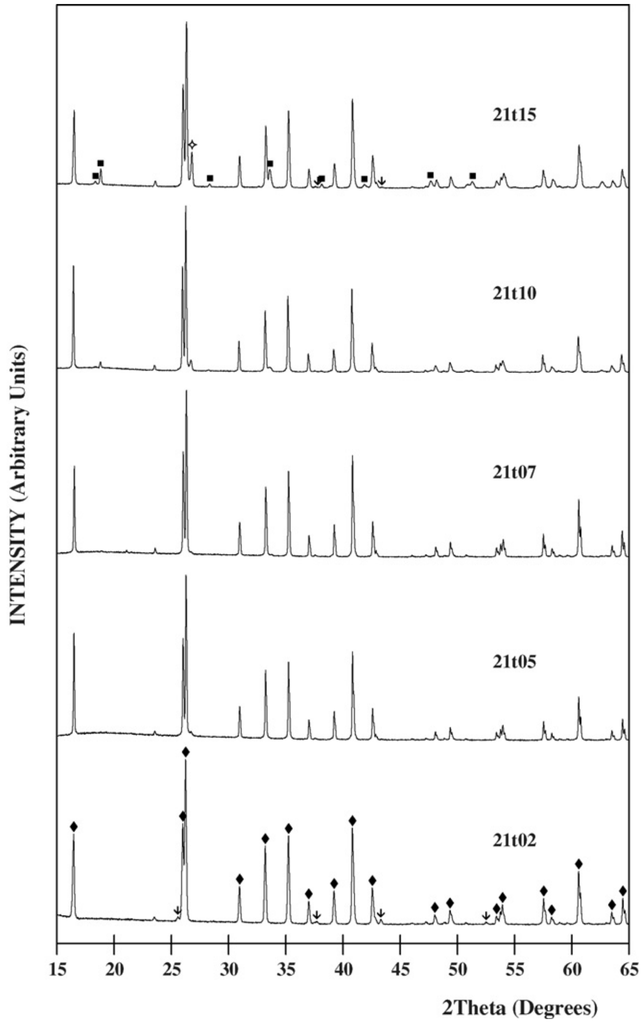

Fig. 1. XRD patterns of titanium oxide-doped 2:1 mullites thermally treated at 1600 °C for 2 h (♦: mullita, ↓: alumina, ✧ : quartz and ■: pseudobrookite).

oxide, 32t15 and 21t15. The spinel phase was not detected in specimens processed at temperatures 1100 °C and higher. Gels with nominal titanium oxide amounts up to $x = 0.07$ thermally treated in the range between 1100 and 1600 °C, resulted in a single crystalline phase with mullite structure. XRD patterns of TiO_2-doped mullite from 2:1 series gels heated at 1600 °C for 2 h is shown in Fig. 1. For specimens from both gel series with dopant amounts larger than $x = 0.07$, processed at 1600 °C, a small amount of pseudobrookite and an almost indistinguishable amount of rutile were also detected. However, it is to note that even for gels containing larger nominal amount of titanium oxide the amount of crystalline minor phases in specimens obtained at all range of processing temperatures studied was very small. This fact is in agreement with the formation of a solid solution with increasing titanium oxide content into the mullite structure on increasing the nominal amount of TiO_2 in gels. Furthermore, the formation of pseudobrookite as secondary crystalline phase points out that the limit of solubility of TiO_2 in both mullite series will be in the range of compositions between $x = 0.07$ and $x = 0.1$. A straight way to determine the amount of titanium oxide incorporated into the mullite phase is to determine the lattice parameters change with the nominal gel composition up to $x = 0.1$ at a given processing temperature. As an example of both mullite series the evolution of the lattice parameter a versus the final temperature for different titanium-containing 3:2 mullites is shown in Fig. 2. Standard deviations are displayed as vertical bars. In general, the three lattice parameters increase with raising the titanium oxide doping content for a given temperature. This increase is stronger in the range of low temperatures, i.e. between 1100 and 1400 °C, and for compositions between $x = 0.02$ and $x = 0.07$. The lattice parameter variation for larger titanium oxide nominal contents is erratic because mullite is saturated of titania as evidenced by the presence of pseudobrookite and rutile as secondary phases.

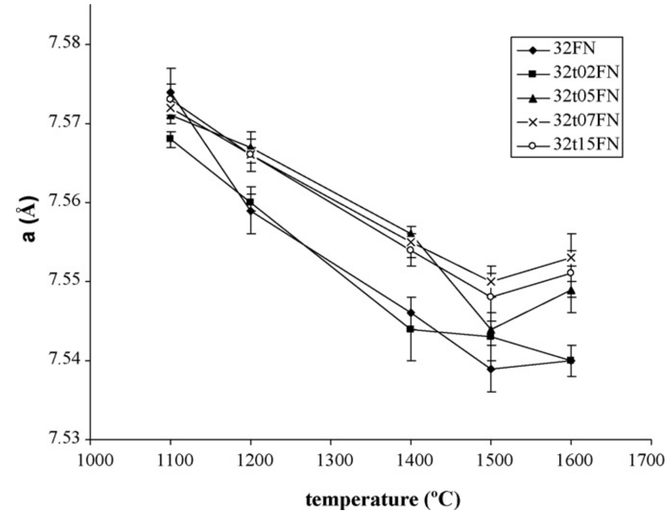

Fig. 2. Variation of parameter a in titanium oxide-containing 3:2 mullites with heating temperature.

The variation of lattice parameters with the process temperature for a given amount of doping is very illustrative. The trend of the parameter a in gels of both series with different titanium amounts is to decrease on increasing the temperature. This behaviour can be understood assuming that the titanium-doped Al_2O_3-rich mullite formed at the first stage with increasing the temperature becomes more siliceous. This process, leading to more siliceous mullite determines the changes of the parameter a with the temperature. On contrast, both parameters b and c hold almost constants on increasing the heating temperature for a given nominal amount of titanium oxide.

The estimates of the limit of solubility of titanium oxide in both types of mullites can be obtained from the representation of the lattice unit-cell volume against nominal content of titanium oxide (in wt%) in samples processed at temperatures between 1400 and 1600 °C. In this range of temperature the replacement of silicon by aluminium is almost completed. As it can be seen in Figs. 3 and 4 in both series heated at 1600 °C the unit-cell volume increases up to around $x = 0.07$ with a constant slope and for larger amounts of titanium a change of the slope occurs. A similar behaviour is observed for specimens heated at 1400 and 1500 °C. Although it is difficult to determine precisely the solubility limit of titanium in mullites, it can be assumed to be in the range $0.07 \leq x \leq 0.075$. Thus, the limit of solubility will

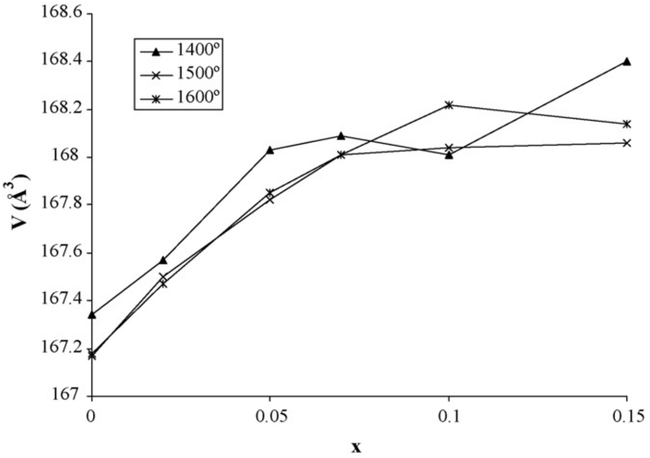

Fig. 3. Lattice volume variation of titanium oxide-containing 3:2 mullites with increasing nominal titanium oxide amounts at different temperatures.

be in the range between 3.8 and 4.1 wt% TiO_2 for 3:2 mullites and between 4.1 and 4.4 for 2:1 (Al_2O_3-richer) mullites. According to these results it can be drawn that the solubility of titanium oxide in both 3:2 and 2:1 mullites is dependent on the mullite composition because both pure mullites have different amount of Al_2O_3. From the about experimental data it is not possible to elucidate the mechanism of formation of these solid solutions based on mullite stable compositions due to the complexity of their crystal-chemistry. Some authors have stated that Ti^{4+} cations enter into mullite by replacement of Al^{3+} in octahedral coordination.[12,27] However, it is known that Ti^{4+} can occupy tetrahedral sites in, for instance, some silicates.[28] To ascertain the mechanism of formation of these solid solutions we are currently determining the structure of both types of Ti-doped mullite solid solutions.

3.2. Infrared spectroscopy of mullites doped with titanium oxide

In order to confirm the titanium oxide amount which can be incorporated into the mullite structure we have recorded the infrared spectra of both titanium oxide-containing 3:2 and 2:1 mullite series thermally treated at 1600 °C. Figs. 5 and 6 display the IR spectra for 3:2 and 2:1 series, respectively. As it can be seen for both series of titanium-doped mullite gels heated at 1600 °C for 2 h, all the characteristic bands of mullite at 1175, 1120, 905, 845, 750 and 460 cm^{-1} are observed.[29] In addition, a very weak absorption band centred at around 650 cm^{-1} is distinguished for compositions with $x = 0.10$ and $x = 0.15$, for which the nominal titanium amount is larger than the solubility limit. As it was mentioned above, in the XRD studies for specimens with the higher contents of titanium oxide, heated at temperatures between 1400 and 1600 °C, aluminium titanate (pseudobrookite) appeared as secondary phase. The IR bands of aluminium titanate prepared using sol–gel techniques has been reported.[30] In the 400–900 cm^{-1} range, two groups of bands in gel precursors heated at 1400 °C can be distinguished, one with a sharp peak at 466 cm^{-1} and the other with peaks at 653, 723 and 843 cm^{-1}. From this set of bands, the only one at 653 cm^{-1} does not overlap the bands from mullite and therefore its presence in the specimens with high titanium content indicates that the solubility limit has been reached. A close look to Figs. 5 and 6, shows an additional absorption in the 640–670 range for specimens with the higher titanium oxide contents of both series, i.e. for the specimens 32t10, 21t10, 32t15 and 21t15. These findings confirm that the limit of solubility of titanium oxide in 3:2 and 2:1 mullites has been exceeded in these specimens.

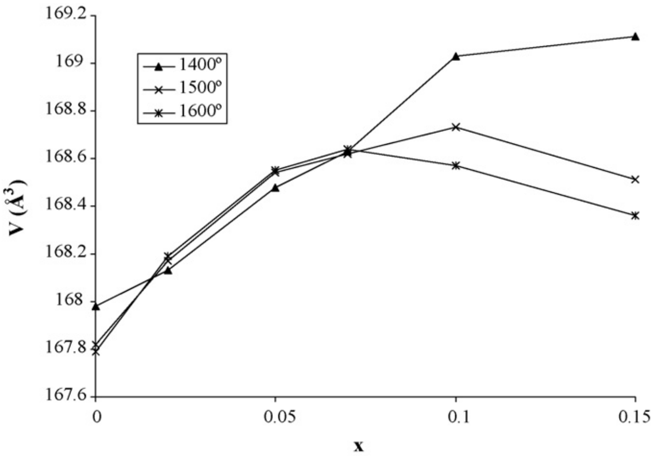

Fig. 4. Lattice volume variation of titanium oxide-containing 2:1 mullites with increasing nominal titanium oxide amounts at different temperatures.

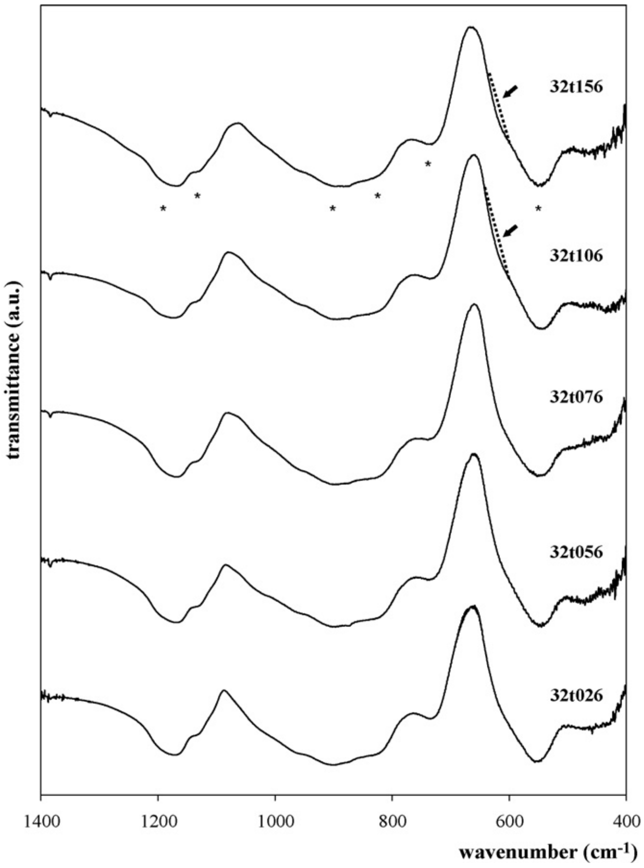

Fig. 5. IR spectra of titanium-oxide containing 3:2 mullites heated at 1600 °C.

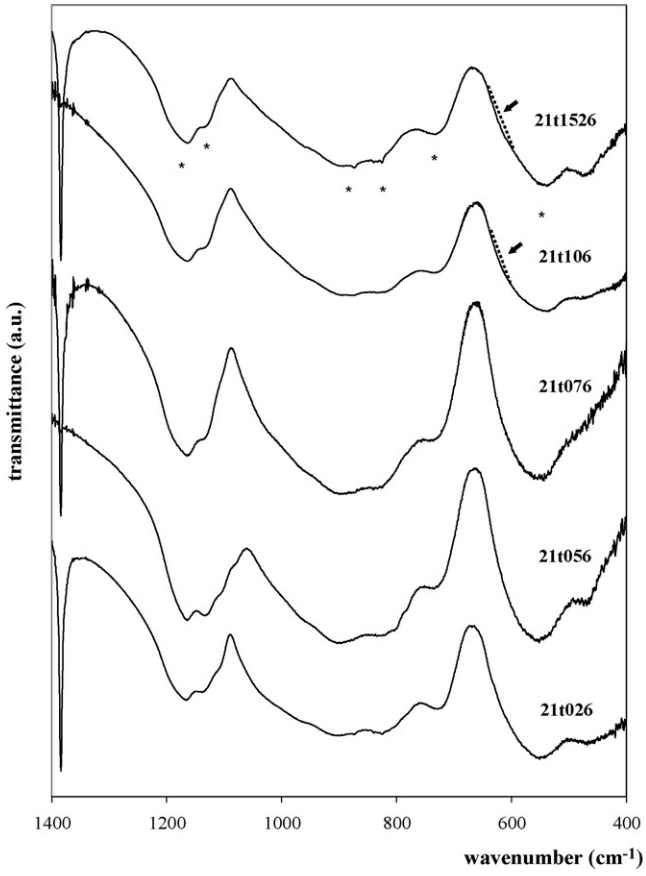

Fig. 6. IR spectra of titanium-oxide containing 2:1 mullites heated at 1600 °C.

3.3. Microstructure of doped mullites

In this section we are going to study the effect of titanium oxide on the anisotropic growth of crystalline grains of mullites from both 3:2 and 2:1 monophasic gels. In this respect, it would be valuable to check firstly whether this anisotropic growth occurs when all the titanium oxide is in solid solution into the mullite structure and, if it is so, to check if the anisotropy is also dependent on the titanium content incorporated into the mullite structure.

Firstly, in order to confirm the amount of TiO_2 incorporated into the doped 3:2 and 2:1 mullite samples we have determined the TiO_2 content in some samples by energy-dispersive X-ray microanalysis. For 21t07 and 21t15 thermally treated at 1600 °C the amounts of TiO_2 were 4.2 and 4.6 wt%, respectively. For the 3:2 series the dopant content was measured only for the specimen 32t07 heated at 1400 °C, being 3.7 wt% TiO_2. Although the difficulty of obtaining accurate values from energy-dispersive microanalysis is well know, these results fit reasonably well with results of analysing the lattice parameters.

From both, lattice parameter analysis and microanalysis results, therefore, we can assume that the limit of solubility of titania for both heated mullite gel series is around $x = 0.07$; so the first point to bring light may be solved by examining the microstructure of 32t07 and 21t07 heated at 1600 °C and compare them with the microstructure of samples with an excess of titanium dioxide, 32t15 and 21t15, heated at the same temperature. Figs. 7–10 show the FESEM images of the grain-level microstructure developed for both doped 3:2 and 2:1 mullites, with $x = 0.07$ and $x = 0.15$, thermally processed at 1600 °C, respectively. As it can be seen in Fig. 7 the 32t07 mullite grains are prismatic with lengths in the range between 500 and 700 nm. On contrast, the microstructure of TiO_2-doped 2:1 mullite, 21t07 (Fig. 8) shows an arrangement of equiaxial grains of sizes in the range between 700 nm and 1 μm. The microstructure of undoped 3:2 and 2:1 mullites obtained from monophasic gels thermally treated at 1600 °C was reported elsewhere[23]; for both compositions equiaxial grains of sizes in

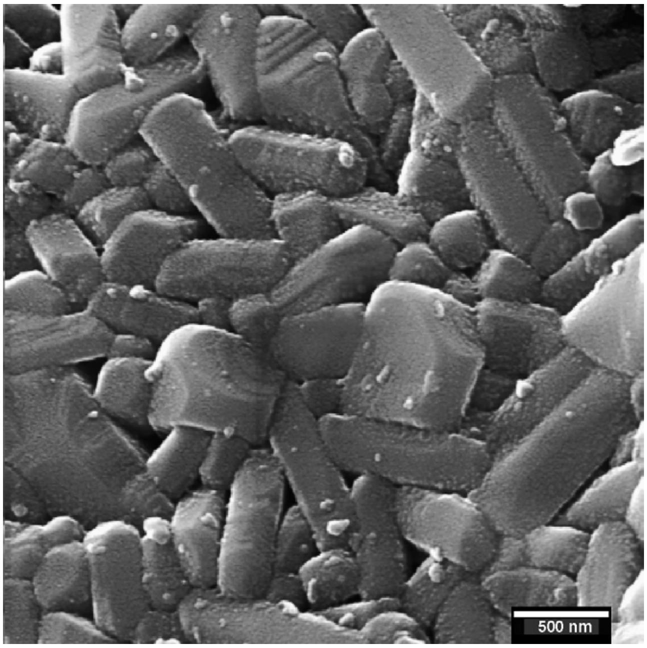

Fig. 7. FESEM micrograph of 32t07 gel heated at 1600 °C for 2 h (bar = 500 nm).

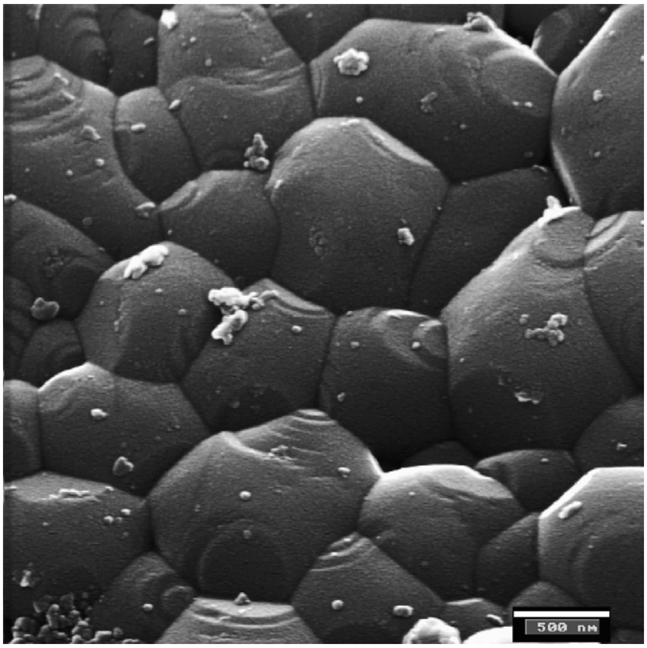

Fig. 8. FESEM micrograph of 21t07 gel heated at 1600 °C for 2 h (bar = 500 nm).

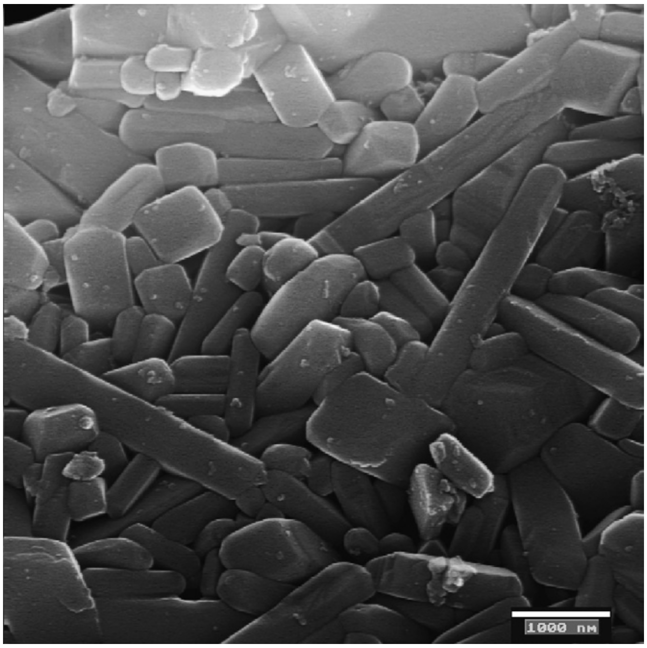

Fig. 9. FESEM micrograph of 32t15 gel heated at 1600 °C for 2 h (bar = 1000 nm).

the range between 500 and 700 nm formed. From the above results it can be drawn that the anisotropy of mullite grains at 1600 °C is almost negligible for titanium-doped 2:1 mullite gels when most of the titanium cation is incorporated into the mullite structure forming a solid solution. For titanium oxide-doped 3:2 mullites and titanium contents below the solubility limit some anisotropy is observed. For these SiO_2-rich nominal compositions a wide arrangement of prismatic grains with an aspect ratio around 3 is observed. From these results it can be drawn that the TiO_2-doped mullite grains, developed from heated titanium oxide-containing single phase 3:2 and 2:1 mullite gels, do not present significant shape anisotropy when the nominal titanium oxide do not exceed the solubility limit. For both titanium oxide-containing mullite series when the nominal amount of titanium oxide is larger than the solubility limit, i.e. when some titanium oxide is available for further reaction at high temperatures, the anisotropy of mullite grains increases. The microstructure of gels 32t15 and 21t15 heated at 1600 °C for 2 h is displayed in Figs 9 and 10. As it can be seen in Fig. 9 very large mullite crystals can be distinguished in TiO_2-doped 3:2 mullites, with aspect ratio larger than 10. For the 2:1 series elongated mullite grains also formed but a part of grains remain almost equiaxial. This behaviour can be explained by smaller content of silica in 2:1 mullite series. These results indicate that the anisotropic growth of mullites is favoured when there is an excess of nominal titanium oxide respect to the limit of solubility and being stronger for the SiO_2-richer (3:2) mullite series. Previous results on the anisotropic growth of titanium oxide doped 3:2 mullites from diphasic gels were reported by Hong and Messing.[13,14] The authors found that titania-doped samples from these diphasic gel precursors contained both equiaxial and elongated grains. The quantity of elongated grains increased as the titania concentration enhanced. From this type of gel precursors with 5 wt% doping strongly elongated mullite grains developed. However, it is to note that XRD pattern of this titania-doped mullite from gel sintered at 1650 °C showed the presence of rutile. This means that the limit of solubility of titanium oxide in mullite had not been reached and therefore some content of unreacted titania could produce regions of lower viscosity even at lower temperatures, that caused the anisotropic grain growth.

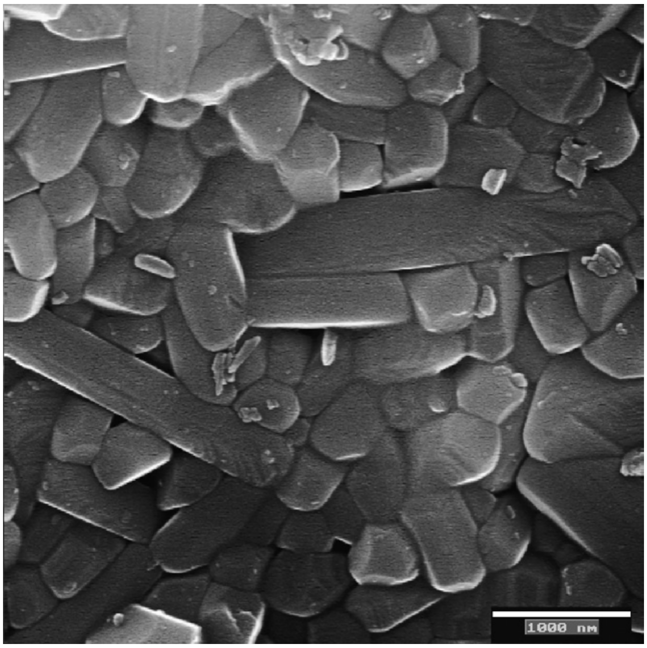

Fig. 10. FESEM micrograph of 21t15 gel heated at 1600 °C for 2 h (bar = 1000 nm).

When comparing these results with our results it may be concluded that the anisotropic growth of mullite crystals, in both diphasic and monophasic 3:2 mullite gel precursors, is very similar. The only difference is that in the diphasic series the formation kinetics of the titanium-doped mullite solid solutions is slow and consequently the unreacted titanium oxide remains in the specimens with nominal compositions smaller than 5 wt% TiO_2. Thus, anisotropic growth is favoured by the low viscosity provided by titania to the residual silica-rich glassy phase. This behaviour is clearly observed for titania-containing 3:2 single-phase mullite gel precursors when the nominal TiO_2 is higher than 5 wt%, because for smaller titania contents all the titanium oxide is incorporated into the mullite structure. For the 2:1 series, there are no reported results for titanium-doped diphasic gels. So, we cannot compare them with similar single-phase gel series. However, it is to be noted that the anisotropic growth is much more reduced. This behaviour may be explained by the relatively smaller silica content of the 2:1 gel series with respect to the 3:2 series. The anisotropic growth is also strongly dependent on the final heating temperature for titanium oxide-containing 3:2 mullite. Figs. 11 and 12 show the microstructure of gels 32t07 and 32t15, respectively, heated at 1400 °C. As it can be seen the grain sizes of mullites with different nominal titanium oxide amount are very similar and are comparable to the sizes displayed by

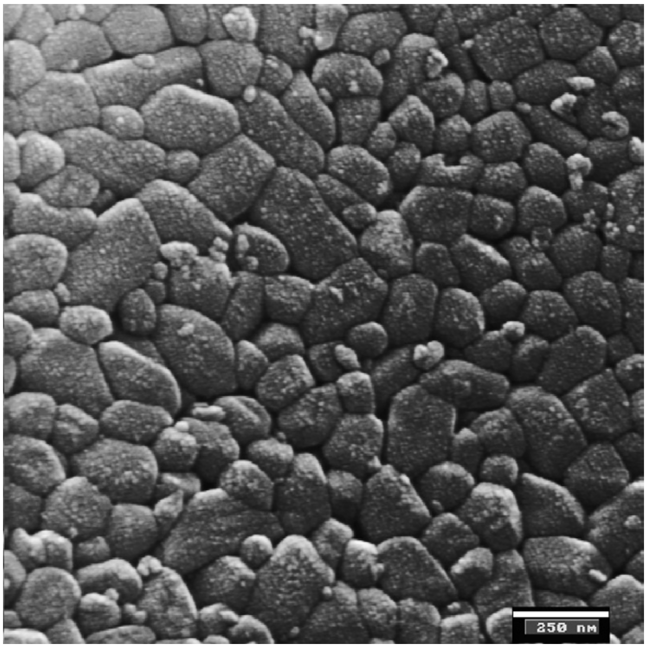

Fig. 11. FESEM micrograph of 32t07 gel heated at 1400 °C for 2 h (bar = 250 nm).

undoped mullites.[24] Likewise, no anisotropic growth is shown in these TiO_2-doped mullite grains. From the above results it can be drawn that the anisotropic growth in titania-doped mullites prepared from single-phase gels takes place when an excess of dopant respect to the solubility limit of titanium oxide in mullites occurs and at sufficiently high temperatures results in appearing of a relatively low viscous glassy phase. The oriented growth is sharper for SiO_2-richer mullites.

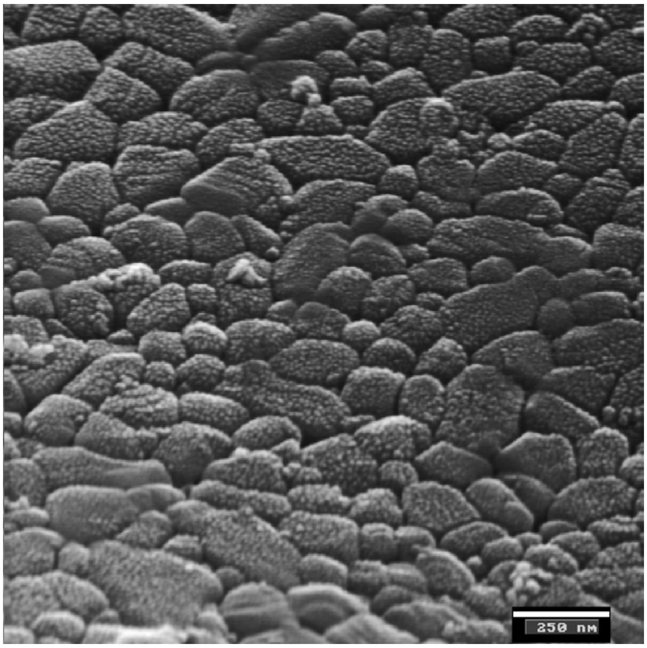

Fig. 12. FESEM micrograph of 32t15 gel heated at 1400 °C for 2 h (bar = 250 nm).

4. Conclusions

Single-phase gels of 3:2 and 2:1 mullites with increasing TiO_2 contents have been prepared and thermally treated at temperatures up to 1600 °C. XRD of heated gels showed the formation of titanium oxide-containing solid solutions with mullite structure for both series of gels. $TiAl_2O_5$ and TiO_2 were detected as minor secondary phases after reaching the maximum incorporation of titanium into the mullite structure. Lattice parameter variation allowed estimating that the limit of solubility of titanium oxide was in the ranges 3.8–4.1 and 4.1–4.4 wt% TiO_2 for 3:2 and 2:1 mullites, respectively. Microstructural examination showed that anisotropic growth of mullite crystals occurred only for gel precursor compositions with nominal titanium oxide contents exceeding the solubility limit. The anisotropic growth took place mainly in TiO_2-doped 3:2 mullites, while in 2:1 the quantity of grains with directional growth was small. Finally, it can be pointed out that the anisotropic growth was dependent on temperature and occurred only at temperatures higher than 1400 °C.

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