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Thermal evolution and structural study of 2:1 mullite from monophasic gels

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Abstract

Single phase mullite gels with composition $2Al_2O_3{\cdot}SiO_2$ (2:1) were prepared by the slow hydrolysis method using aluminium nitrate nonahydrate and tetraethylorthosilicate as reagents. The evolution to mullite from gels was studied by infrared (IR) spectroscopy and X-ray diffraction (XRD). Gels thermally treated under fast schedules showed mullite formation below 900 °C. Compositional and microstructural changes in 2:1 mullites through the range of temperature from 900 to 1600 °C were determined by the measurement of lattice parameters and field emission scanning electron microscopy. The alumina-rich mullites formed at low temperatures become almost the nominal 2:1 at 1600 °C. This result is consistent with available thermodynamic data for mullite formation from alumina and silica. Microstructural examination indicated an almost constant grain size for mullite from 900 to 1600 °C.

Keywords: Sol–gel processes; Microstructure-final; X-ray methods; Mullite

1. Introduction

Mullite-based materials have received much attention in the last decades. It is an essential component in traditional ceramic materials such as porcelain, but is also a crucial component for ceramic materials with specific properties and applications.[1–3] Mullite is the only crystalline phase within the binary system Al_2O_3–SiO_2.[4,5] In fact, it is a solid solution with stoichiometry $Al_2[Al_{2+2x}Si_{2-2x}]O_{10-x}$, with $0.17 \leq x \leq 0.5$.[6,7] From a general view, the interval of composition of mullite ranges from $3Al_2O_3{\cdot}SiO_2$ to $2Al_2O_3{\cdot}SiO_2$ (hereafter denoted as 3:2 and 2:1). However, as far as we know, most papers in the literature have dealt with synthetic and microstructural aspects of silica-rich mullite, i.e. 3:2.[8–11]

Sol–gel techniques have been used to prepare monophasic and diphasic mullite gels.[12–16] Single phase gels have been prepared by two distinct methods. The first, named all-alkoxide, is based on the controlled hydrolysis of aluminium and silicon alkoxides. In the second, named semialkoxide method, the aluminum source is a salt, usually nitrate nonahydrate. It has been proved that when using all reagents as alkoxides, it is quite difficult to control the reactivity because both aluminum and silicon alkoxides have very different hydrolysis rates and some unhomogeneity is reached. However, with the semialkoxide method, higher homogeneity is attained, as evidenced by the lower temperature formation of mullite, at around 1000 °C.[14–16] An important aspect is the effect of the subsequent thermal treatment of gels on the mullite formation sequence, as has been evidenced in the literature.[10]

The mullite of composition 2:1 is usually obtained by cooling from a melt or by directional solidification.[17,18] There are relatively few reports in the literature on the formation of mullite 2:1 by using sol–gel techniques. The thermal evolution of the Al_2O_3-rich (2:1) mullite colloidal gel was investigated some years ago.[19] The different crystallization path in monophasic gel precursors has been attributed to the influence of synthesis conditions.[8–10,12,14] However, these studies were carried out with 3:2 mullite gel precursors. Reports on the reaction sequence and microstructural evolution of

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2:1 mullite from real 2:1 monophasic gels are very few.[15] Vilminot et al. claimed that, at around 1000 °C, pure tetragonal mullite form is achieved only for gel of the semialkoxide route, whereas spinel is obtained only from of the all-alkoxide route.[15] This has been attributed to the formation of local alumina-rich heterogeneities related with the difference of reactivity of aluminum and silicon alkoxides. However, it is to be mentioned here that our previous results indicate that not only the synthetic procedure (nature of reagents, solvent, temperature and time reaction, catalizer) is important in the mullite formation, but also the thermal treatment is crucial in the crystallization scheme of gels.

Since few experimental results have been reported regarding the mullitization of 2:1 nominal mullite gels prepared by the semialkoxide method, it seems interesting to study the formation of these mullites from monophasic gels prepared by this method. The main advantage associated with the semialkoxide synthetic procedure would be that a high homogeneity can be reached in the precursor gels. Therefore, this paper aims at examining the crystallization path in this alumina-rich mullite monophasic gel. Also, the microstructural evolution of the 2:1 mullites obtained during the thermal treatment of gel precursors will be reported.

2. Experimental procedure

2.1. Preparation of specimens

Monophasic gels with stoichiometry $2Al_2O_3{\cdot}SiO_2$ were prepared from aluminium nitrate nonahydrate and tetraethylorthosilicate (TEOS), both reagents from Merck. The procedure for synthesizing gels was as follows: 28.4 g of aluminum nitrate were dissolved in 36.0 ml of absolute ethanol (EtOH) under reflux. To the above solution, the stoichiometric amount of TEOS dissolved in EtOH was added and the resulting solution was kept under reflux for 7 days. The amount of H_2O for hydrolysis and condensation of TEOS and aluminum salt was provided by the aluminun nitrate nonahydrate. The molar ratio Al^{3+}:EtOH in the final solution was 1:12. After refluxing, the resulting mixture was poured into a beaker, covered with a holed parafilm layer and aged for around 1 month. The finally obtained gel was dried at 60 °C for 12 h followed by further drying at 120 °C for 12 h. Cylindrical pellets of loosely pressed gel powders were thermally processed at several temperatures between 900 and 1600 °C, holding the sample for 2 h at the final temperature. The heating rate was 30 °C/min in all thermal processings.

2.2. Techniques of characterization

In order to follow structural and chemical changes from gel to final mullite material as-prepared and thermally treated gels were studied by the following techniques: Differential thermal analysis (Model Pyris Diamond TG/DTA, Perkin-Elmer, Norwalk, Connecticut, U.S.A.) was carried out in air with platinum liners, using a heating rate of 10 °C/min.

Infrared absorption spectra (Model 882, Perkin-Elmer Ltd., Beaconsfield, Buckinghamshire, UK) were obtained in the range 1400–400 cm^{-1} using the KBr pellet method.

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

The microstructure of the as-prepared and thermally treated samples was observed by field emission scanning electron microscopy working at 20–30 kV (Model S-4100, Hitachi Ltd., Tokyo, Japan). 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.

3. Results and discussion

3.1. Crystallization of gels

Differential thermal analysis curve for 2:1 mullite gel, prepared by the previously described procedure, is shown in Fig. 1. As it can be seen, a unique peak around 980 °C is displayed. X-ray difractogrammes of cooled specimens from DTA runs at 980 and 1050 °C confirms that crystalline mullite is formed as the unique crystalline phase. It is to be noted that in colloidal (i.e. diphasic) mullite gels a further small, exothermic peak appears at ∼1200 °C, associated with the reaction between the spinel, previously formed, with the

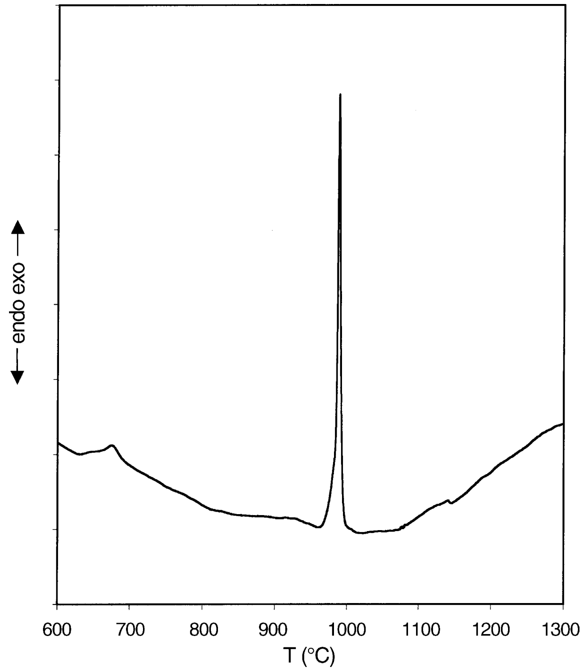

Fig. 1. DTA curve for 2:1 mullite gel heated at 10 °C/min.

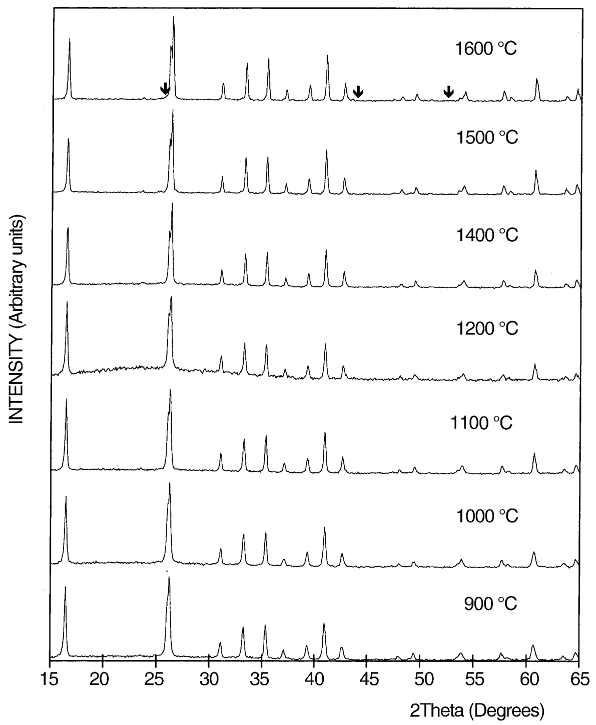

Fig. 2. XRD patterns of 2:1 mullite gels heated at different temperatures for 2 h (↓ is α-Al_2O_3).

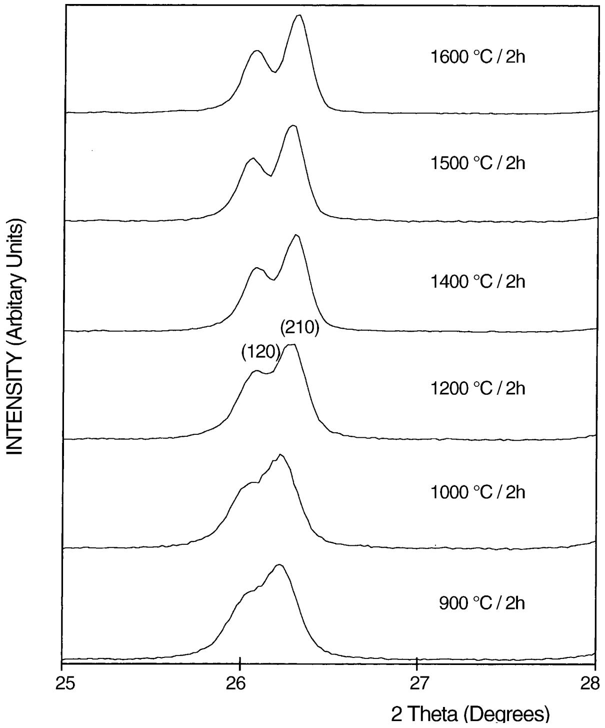

Fig. 3. Splitting of peaks (1 2 0) and (2 1 0) in XRD of 2:1 heated gels with increasing temperature.

silica gel.[8] So, we can consider the precursor gels here synthesized as single phase (i.e. monophasic gels). In order to follow the structural evolution of the single phase, the mullite gel precursors were heated by a relatively fast thermal treatment, at 30 °C/min. X-ray diffractograms of heated products at different temperatures between 900 and 1600 °C for 2 h are shown in Fig. 2. As it can be seen, mullite is already formed after 2 h at 900 °C. It is also to notice that in the mullite formed at as low temperature as 900 °C, a clear splitting of peaks (1 2 0) and (2 1 0) can already be seen. The splitting evolution from mullite gels fast heated at 900 °C up to 1600 °C is displayed in Fig. 3. The path of mullite crystallization during heating, with a rate of 30 °C/min at 900 °C, reveals direct orthorhombic mullite formation from an X-ray amorphous monophasic gel precursor. On increasing the temperature, this alumina-rich phase reacts with silica to form more orthorhombic mullite, i.e. with a higher content of silica.

The crystallization scheme of mullite from molecular gel precursors has been related to the presence of local heterogeneities as previously depicted by Huling et al.[10] Their compositions and relative proportions influence the evolution of the sample at the temperature of the first exotherm, i.e. around 980 °C. Thus, if the local composition of heterogeneities exceeds 71 mol% Al_2O_3, spinel crystallization is induced as well as mullite.[15] From the above results, it is inferred that no large, local heterogeneities occur in gel precursors and, consequently, even at as low temperature as 900 °C, the first crystallized mullite is orthorhombic.

3.2. Infrared spectra of as-prepared and thermally treated gels

In order to follow the qualitative, structural and compositional evolution of the formed mullites with the increasing temperature of the thermal treatment, the IR spectra of dried and heated gels are shown in Fig. 4.

Comparison of the IR spectra of dried and heated gels at 900 °C confirms the XRD finding that mullite is already formed. The IR bands of nitrate at 1380 and 880 cm^{-1} found in the dried gel disappear in the heated gels.[9] The decomposition of nitrates must be complete at around 500 °C. In addition, the dried gel displays broad, overlapping bands, which indicate a disordered structure. After heating at 900 °C, all the characteristics bands of mullite at 1175, 1120, 905, 845, 750 and 460 cm^{-1} are observed. On increasing the heating temperature, the bands become stronger. The relative chemical composition of the mullite obtained at different temperatures has been related with the relative intensity of bands centered at 1130 and 1160 cm^{-1}.[20,21] Okada et al. and Cameron claimed that for Al_2O_3-rich mullites, the band at 1130 cm^{-1} is stronger than the one at 1160 cm^{-1}. In Fig. 4, it can be observed that a continuous increase in the intensity ratio of bands at 1160 and 1130 cm^{-1} with the increase of the heating temperature, so the formed mullites become richer in SiO_2. This is in agreement with the previous splitting of peaks with Miller indices of (1 2 0) and (2 1 0) found in the XRD results.

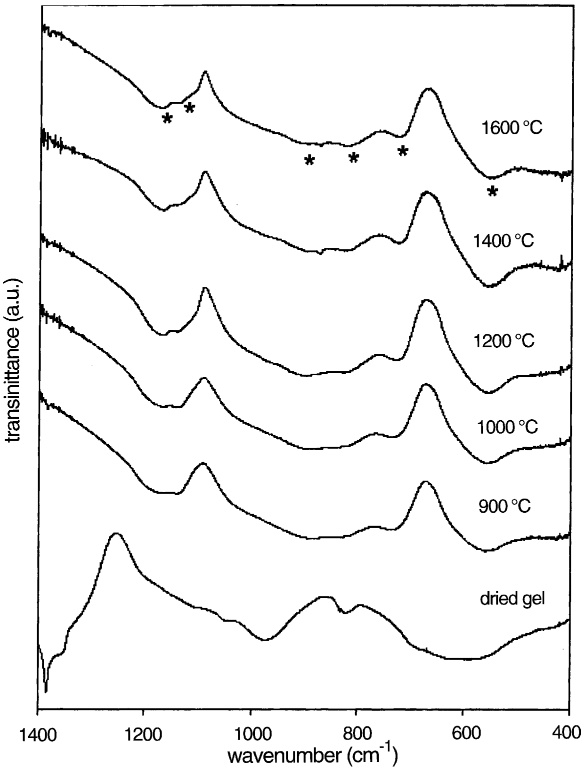

Fig. 4. IR spectra of 2:1 mullite gels heated at different temperatures for 2 h ((✱) is mullite).

3.3. *Lattice parameters and composition of 2:1 mullites*

Lattice parameters of mullite obtained from gels heated at increasing temperatures between 900 and 1600 °C, with a heating rate of 30 °C/min and 2 h soaking time at the final temperature, are displayed in Table 1. As can be seen, parameters *a* and *b* decrease with increasing temperature whereas *c* enhances slightly. With respect to the cell volume, the decrease is produced in two steps at two temperatures, i.e. at 1000 °C and from 1200 to 1600 °C. The decrease of the parameter *a* has been related with the Al_2O_3 amount in crystalline mullite.[6,14,22] The general trend is, the larger *a* parameter the Al_2O_3-richer mullite. From a least-squares fit to Cameron's data, a relationship between the lattice parameter *a* (in Å) and the mole fraction of alumina in the mullite $X(Al_2O_3)$ was inferred by Gerardin et al.[14]:

$$a = 7.2232 + 0.537\,X(Al_2O_3) \qquad (1)$$

Table 1
Lattice parameters of gel 2:1 thermal treated at several temperatures for 2 h under heating rate of 30 °C/min

(°)	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)
900	7.5910 ± 0.0023	7.6893 ± 0.0020	2.8836 ± 0.0003	168.32
1000	7.5865 ± 0.0019	7.6882 ± 0.0017	2.8838 ± 0.0003	168.02
1100	7.5828 ± 0.0022	7.6832 ± 0.0019	2.8841 ± 0.0004	168.03
1200	7.5740 ± 0.0043	7.6838 ± 0.0037	2.8880 ± 0.0007	168.07
1400	7.5771 ± 0.0019	7.6817 ± 0.0017	2.8861 ± 0.0003	167.98
1500	7.5712 ± 0.0022	7.6816 ± 0.0019	2.8856 ± 0.0004	167.82
1600	7.5680 ± 0.0007	7.6839 ± 0.0006	2.8854 ± 0.0001	167.79

Table 2
Amount of Al_2O_3 in mol% calculated from the *a* lattice parameters of 2:1 mullite gels heated at different temperatures between 900 and 1600 °C

Temperature (°C)	Gerardin et al., Eq. (1)	Ban et al. Eq. (2)
900	68.5	67.3
1000	67.7	66.7
1100	67.0	66.1
1200	65.3	64.9
1400	65.9	65.3
1500	64.8	64.5
1600	64.2	64.0

Ban and Okada proposed a new method for estimating the chemical composition of mullite by determining the chemical composition through structural refinements by the X-ray diffraction Rietveld method.[22] The relationship is represented by the following formula:

$$Al_2O_3(\text{mol\%}) = 1443 \times (\text{length of } a \text{ axis}) - 1028.06; \quad (a \text{ is in nm}) \qquad (2)$$

The amounts of Al_2O_3 in mol% calculated from the *a* lattice parameters of 2:1 mullite gels heated at different temperatures between 900 and 1600 °C, using the above mentioned Eqs. (1) and (2), are displayed in Table 2. Thus, for gels heated at low temperatures, i.e. between 900 and 1200 °C, the mullite crystalline phase formed is Al_2O_3-richer than the nominal starting 2:1 composition. The Al_2O_3 (mol%) obtained from Eqs. (1) and (2) at 900 °C are 67.3 and 68.5, respectively. At 1100 °C, the Al_2O_3 molar percentages are 66.1 (Eq. (1)) and 67.0 (Eq. (2)). However, mullite at the final higher temperatures is poorer in Al_2O_3 than the starting nominal composition. For instance, at 1600 °C, the Al_2O_3 mol% calculated from Eqs. (1) and (2) are 64.0 and 64.2, respectively. This fact indicates that a small amount of alumina, as secondary crystalline phase, is present as well as mullite. In this respect, it is to mention that in the XRD pattern of the gel 2:1 heated at 1600 °C are detected very small peaks at around 25.54, 43.88 and 52.48° (2*θ*) associated with the presence of α-Al_2O_3 (Fig. 2). These diffraction peaks are not distinguished in the gel heated at 1500 °C. It is to be noted that the calculated amount of Al_2O_3 for gels heated at 1600 °C, around 64.1, is consistent with the one obtained from the alumina–silica phase diagram proposed by Klug et al. for a starting gel with composition of mullite 2:1.[23] This fact indicates that the starting gel is highly reactive and at least at high temperatures, the set of phases is very close to the one at the equilibrium.

3.4. *Microstructural evolution of mullite gels*

In order to evidence microstructural features of mullites 2:1 at different final temperatures of thermal treatments, FESEM micrographs of 2:1 mullite gels heated at 900 and

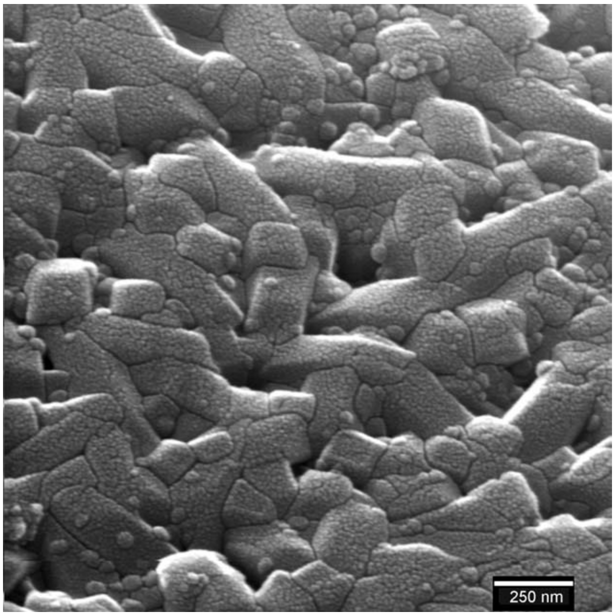

Fig. 5. FESEM micrograph of gel 2:1 heated at 900 °C for 2 h (bar = 250 nm).

1600 °C for 2 h are displayed in Figs. 5 and 6. It can be seen that mullite grains at 900 °C are smaller than 250 nm. It is also evident that no great change in grain size was produced after heating gels at 1600 °C. Thus, as it can be seen in Fig. 6, the microstructure formed from 2:1 monophasic gels fast heated at 1600 °C consists of almost equigranular mullite grains about 250–500 nm in size.

It is to be noted that there are no differences in size and shape of grains for both final mullites in the range of stable compositions, i.e. 3:2 and 2:1, prepared by the described synthetic procedure. In Fig. 7 is shown the microstructure after heating mullite gels with composition 3:2 at 1600 °C for 2 h. Almost the same picture of equigranular mullite grains sized between 250 and 500 nm is clearly observed. From the above micrographs, no acicular grains are present at 1600 °C. The presence of grains with acicular shape has been associated with the presence of a liquid phase. Therefore, it can be assumed that no liquid phase is formed on heating 3:2 and 2:1 monophasic mullite gels at 1600 °C.

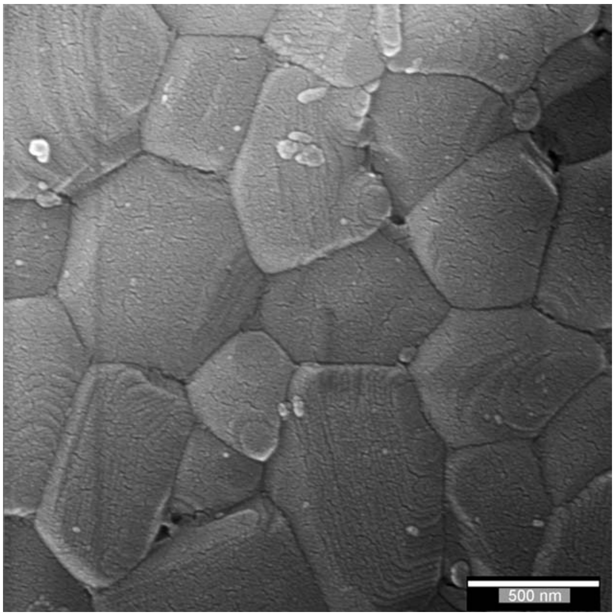

Fig. 6. FESEM micrograph of gel 2:1 heated at 1600 °C for 2 h (bar = 500 nm).

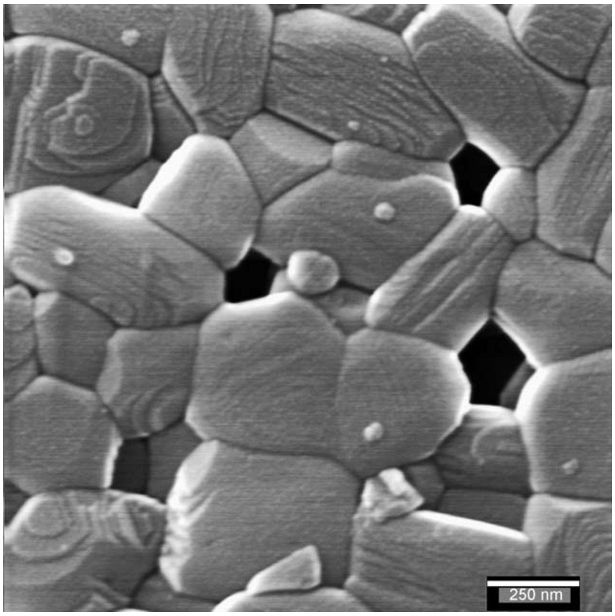

Fig. 7. FESEM micrograph of gel 3:2 heated at 1600 °C for 2 h (bar = 250 nm).

From the above facts, it can be drawn that the formation of mullite 2:1 prepared from monophasic gel takes place without any chemical interdifussion. The process occurs by a rearrangement of the atoms on heating and the stable solid solution range of mullite in the Al_2O_3–SiO_2 binary system will determine the final mullite composition.

4. Conclusions

Monophasic mullite gel precursor with nominal composition 2:1 were prepared by the semialkoxide method and thermal treated at several temperatures between 900 and 1600 °C for 2 h. XRD patterns and IR spectra confirmed the formation of Al_2O_3-rich mullite as the only crystalline phase after heating gels at 900 °C for 2 h. In addition, the crystallized mullite became SiO_2-richer on increasing the final temperature. The Al_2O_3 (mol%) obtained from Gerardin et al.[14] and Ban et al.[22] equations indicated that the final mullite obtained at 1600 °C was slightly less aluminous than the corresponding to the nominal stoichiometry 2:1 (66.6 mol% Al_2O_3). This result was consistent with available thermodynamic data for mullite formation from alumina and silica. The microstructural evolution indicated an almost constant grain size for mullite from 900 to 1600 °C.

Acknowledgments

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References

1. Aksay, I. A., Dabbs, D. M. and Sarikaya, M., Mullite for structural, electronic and optical applications. *J. Am. Ceram. Soc.*, 1991, **74**, 2343–2358.
2. Andrews, L. J., Beall, G. H. and Lempicki, A., Luminescence of Cr^{3+} in mullite transparent glass ceramics. *J. Lumin.*, 1986, **36**, 65–74.
3. Iqbal, Y. and Lee, W. E., Microstructural evolution in triaxial porcelain. *J. Am. Ceram. Soc.*, 2000, **83**, 3121–3127.
4. Aksay, I. A. and Pask, J. A., Stable and metastable equilibria in the system Al_2O_3–SiO_2. *J. Am. Ceram. Soc.*, 1975, **58**, 507–512.
5. Klug, F. J., Prochazka, S. and Doremus, R. H., Alumina–silica phase diagram in the mullite region. *J. Am. Ceram. Soc.*, 1987, **70**, 750–759.
6. Cameron, W. E., Mullite a substituted alumina. *Am. Miner.*, 1977, **62**, 747–755.
7. Angel, R. A. and Prewitt, C. T., Crystal structure of mullite: a re-examination of the average structure. *Am. Miner.*, 1986, **71**, 1476–1482.
8. Pask, J. A. and Tomsia, A. P., Formation of mullite from sol-gel mixtures and kaolinite. *J. Am. Ceram. Soc.*, 1991, **74**, 2367–2373.
9. Li, D. X. and Thomson, W. J., Mullite formation kinetics of a single-phase gel. *J. Am. Ceram. Soc.*, 1990, **73**, 964–969.
10. Huling, J. C. and Messing, G. L., Chemistry-crystallization relations in molecular mullite gels. *J. Non-Cryst. Solids*, 1992, **147–148**, 213–221.
11. Pask, J. A., Zhang, X. W., Tomsia, A. P. and Yoldas, B. E., Effect of sol–gel mixing on mullite microstructure and phase equilibria in the α-Al_2O_3–SiO_2 system. *J. Am. Ceram. Soc.*, 1987, **70**, 704–707.
12. Selvaraj, U., Komarnemi, S. and Roy, R., Structural differences in mullite xerogels form different precursors characterized by ^{27}Al and ^{29}Si MASNMR. *J. Solid State Chem.*, 1993, **106**, 73–82.
13. Sales, M. and Alarcón, J., Synthesis and phase transformations of mullites obtained from Al_2O_3–SiO_2 gels. *J. Eur. Ceram. Soc.*, 1996, **16**, 781–789.
14. Gerardin, C., Sundaresan, S., Benziger, J. and Navrotsky, A., Structural investigation and energetics of mullite formation from sol–gel precursors. *Chem. Mater.*, 1994, **6**, 160–170.
15. Parmentier, J. and Vilminot, S., Influence of synthesis and composition on mullite crystallization. *Chem. Mater.*, 1997, **9**, 1134–1137.
16. Taylor, A. and Holland, D., The chemical synthesis and crystallisation sequence of mullite. *J. Non-Cryst. Solids*, 1993, **152**, 1–17.
17. Pask, J. A., Critical review of phase equilibria in the Al_2O_3–SiO_2. In *Ceramic Transactions, Mullite and Mullite Matrix Composites*, *6*, ed. S. Somiya, R. F. Davis and J. A. Pask. American Ceramic Society, Westerville, 1990, pp. 1–14.
18. Mitchel, D., Mazerolles, L. and Portier, R., Directional solidification in the alumina–silica system microstructures and interfaces. In *Ceramic Transactions, Mullite and Mullite Matrix Composites*, *6*, ed. S. Somiya, R. F. Davis and J. A. Pask. American Ceramic Society, Westerville, 1990, pp. 435–448.
19. Osendi, M. I. and Miranzo, P., Thermal evolution and sintering behavior of a 2:1 mullite gel. *J. Am. Ceram. Soc.*, 1997, **80**, 1573–1578.
20. Okada, K. and Otsuka, N., Characterization of the spinel phase from SiO_2–Al_2O_3 xerogels and the formation process of mullite. *J. Am. Ceram. Soc.*, 1986, **69**, 652–656.
21. Cameron, W., Composition and cell dimensions of mullite. *Am. Ceram. Soc. Bull.*, 1977, **56**, 1003–1011.
22. Ban, T. and Okada, K., Structure refinement of mullite by the Rietveld method and a new method for estimation of chemical composition. *J. Am. Ceram. Soc.*, 1992, **75**, 227–230.
23. Klug, F. J., Prochazka, S. and Doremus, R. H., Alumina–silica phase diagram in the mullite region. In *Ceramic Transactions, Mullite and Mullite Matrix Composites*, *6*, ed. S. Somiya, R. F. Davis and J. A. Pask. American Ceramic Society, Westerville, OH, 1990, pp. 15–43.