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Synthesis and sintering of pre-mullite powders obtained via carbonate precipitation

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Abstract

Ultrafine pre-mullite powders, which yield mullite at high temperatures, have been prepared from colloidal silica and aluminium nitrate via carbonate coprecipitation and followed by calcination. The chemical and structural evolutions of the as-prepared precipitation powder during thermal treatment were studied and the sinterability of pre-mullite powders were investigated. The as-prepared powders are comprised of ammonium aluminum carbonate hydroxide and amorphous silica, which convert to mullite via the Al–Si spinel phase at 1250 °C. Calcination of the as-prepared powders at 1000 °C gives a very active powder which can be reactively sintered to 98.2% theoretical density at 1550 °C. The sintered body possesses a relatively uniform chemical composition with Al_2O_3/SiO_2 mole ratio of 1.48 and exhibits a very fine interlocking equiaxed and polygonal grain morphology with grain size of 100–200 nm.

Keywords: A. Powders: chemical preparation; A. Sintering; D. Mullite

1. Introduction

Mullite ($3Al_2O_3\cdot 2SiO_2$) has been considered to be an important material for advanced structural applications owing to its unique combination of properties such as good mechanical strength, excellent thermal shock resistance, high creep resistance, low thermal expansion, as well as good chemical and thermal stability [1–5]. The conventional synthesis of mullite, which is performed by the reaction of mixed alumina and silica powders or aluminosilicate mineral precursors, requires very high temperatures (1600–1700 °C) and long reaction times to complete the solid-state reaction, and the products commonly have variable composition so that sintered bodies contain an excess of alumina or silica as a second phase [5–7]. In order to overcome these problems, considerable attempts have been made to prepare mullite with more uniform composition and at lower temperatures from pre-mullite powders prepared via wet chemical processes such as coprecipitation, sol–gel, spray-drying and hydrothermal methods [8–11]. Among these, the coprecipitation method is a relatively convenient way for pre-mullite powder preparation. It can provide good mixing of the starting materials and produce pre-mullite powders with good chemical homogeneity, high chemical purity and fine grain particle size, which are the most important factors in the preparation of dense sintered mullite bodies having a stoichiometric composition and homogeneous microstructure.

As for wet chemical processes, mullite can be formed via different routs according to the kinds of starting materials and processing conditions which may affect the mixed state of aluminium and silicon species in the initially formed solid-state and also influence the course of mullitization. Raw materials of two alkoxides give an amorphous mixture of aluminium and silicon species. In the cases of the combination of an alkoxide and an inorganic salt or two inorganic salts (or sols), silicon species is usually present in the mixed state as amorphous, while aluminium species may be amorphous, boehmite or other forms depending on the aluminium-bearing starting material used and reaction reagents added.

In the present work, ammonium carbonate has been employed as the precipitant to synthesise mullite precursors from a mixed solution of aluminum nitrate and colloidal silica.

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Under the processing condition used, aluminum species was precipitated in the as-prepared state as ammonium aluminum carbonate hydroxide (AACH) together with amorphous silica. Well-sinterable ultrafine pre-mullite powders that could densify to >98% of the theoretical density at 1550 °C were obtained by calcining the as-prepared precursors at temperatures of 1000 °C. The present article addresses the preparation and characterization of the pre-mullite powders, as well as its sintering behavior.

2. Experimental procedure

Aluminum nitrate nonahydrate, $Al(NO_3)_3 \cdot 9H_2O$ >99% purity, ammonium carbonate ($(NH_4)_2CO_3$, analytical grade), and colloidal silica, derived from water glass (mole ratio of 3.4, technical grade) by an ion exchange method, were used as starting materials. The precursor precipitate was made by adding 200 mL of a 0.30 mol L^{-1} (for Al^{3+}) mixed solution of aluminum nitrate and colloidal silica (in the mole ratio $3Al^{3+}:Si^{4+}$) dropwise into 400 mL of a 1.5 mol L^{-1} ammonium carbonate under rapid stirring at 40 ± 1 °C, with a subsequent aging period of 1 h. The resulting suspension was filtered using suction filtration, washed thoroughly with distilled water, and then mixed with n-butanol and distilled to remove water as azeotrope. The precursor powder obtained after azeotropic distillation was calcined at various temperatures for 2 h with an air atmosphere.

In order to measure the crystalline phase and thermal behavior of the as-prepared powder, some wet precipitate obtained after filtration and water washing was dried at room temperature under vacuum.

Differential thermal analysis/thermogravimetry (DTA/TG) was conducted using Netzsch STA 409 PC/PG thermal analyzer in flowing Ar (60 mL min^{-1}) at a heating rate of 10 °C min^{-1}. Phase identification was performed by X-ray diffraction (XRD) with a X'Pert PRO X-ray powder diffractometer, with Cu-K_a radiation (λ = 1.5418 Å). The lattice parameters of mullite were calculated by the least-squares method using a computer program, selecting 12 XRD peaks (2θ between 16 and 70°). The particle morphology and size were observed by transmission electronic microscopy (TEM) using a Jeol JEM-2010 electron microscope. Specific surface area was measured via the Brunauer–Emmett–Teller (BET) method with nitrogen absorption using an Micromeritics ASAP 2000 automated volumetric analyzer. Samples were degassed at 150 °C for 2 h under vacuum prior to analysis.

For sintering studies, the powders, obtained by calcining the azeotropically distilled powders at 800 °C, 1000 °C and 1250 °C for 2 h and ball-milled for 4 h in a nylon jar using zirconia balls, were uniaxially dry-pressed at 50 MPa and subsequently isostatically pressed at 250 MPa. The powder compacts were sintered in air at various temperatures from 1250 °C to 1600 °C for 2 h with a heating rate of 6 °C min^{-1} and a cooling rate of 25 °C min^{-1}. The bulk densities of the sintered compacts were measured by the Archimedes' method. Relative bulk densities were calculated by taking the theoretical density of mullite as 3.17 g cm^{-3}. The microstructure of the sintered specimens were observed by scanning electron microscopy (SEM) on polished and thermally etched (1500 °C, 1 h) samples using a Jeol JSM-6700 electron microscope. Chemical analyses were performed on a polished section with energy dispersive X-ray spectroscopy (EDS).

3. Results and discussion

3.1. Phase evolution of the precursor

The as-prepared powder obtained after drying at room temperature showed the XRD pattern of ammonium aluminum carbonate hydroxide (AACH) (Fig. 1(a)), indicating that aluminum and silicon were present in the as-prepared state as AACH ($NH_4Al(OH)_2CO_3 \cdot H_2O$) and amorphous silica ($SiO_2 \cdot xH_2O$), respectively. Fig. 2 shows the TG-DTA curves of the as-prepared powder. There are one endothermic peak and two exothermic peaks occurring up to ~1400 °C, with a total weight loss of ~55%. The endothermic peak, located at ~185 °C, associated with weight loss, was caused by the decomposition of $NH_4Al(OH)_2CO_3$ [12] and the release of CO_2 and molecular water. The TG curve shows ~52% of weight loss up to ~600 °C due to the removal of absorbed water, crystal water, hydroxyl, and the decomposition of $NH_4Al(OH)_2CO_3$. There is almost no further weight change beyond 600 °C. The very broad and diffuse exothermic peak extending from ~600 °C to 1200 °C is associated with the gradual formation of Al–Si spinel in concert with the liberation of heat, and the exothermic peak at 1240 °C corresponds to the transformation of Al–Si spinel to orthorhombic mullite [13], both of which can be confirmed by the XRD results given in Fig. 1. The XRD pattern of the powder calcined at 200 °C shows the presence of pseudoboehmite (AlO(OH)) and amorphous SiO_2 as two discrete phases, this suggests that AACH decomposed into pseudoboehmite at 200 °C. The XRD pattern for the powder calcined at 400 °C shows that pseudoboehmite was transformed

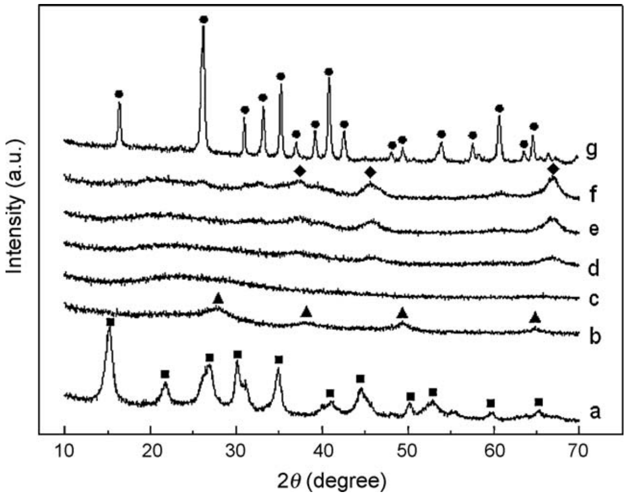

Fig. 1. XRD patterns of the as-prepared powder and powders calcined at various temperatures (a) as-prepared powder, (b) 200 °C, (c) 400 °C, (d) 800 °C, (e) 1000 °C, (f) 1200 °C, and (g) 1250 °C. (■) $NH_4AlO(OH)HCO_3$, (▲) AlO(OH), (◆) Al–Si spinel, and (●) mullite.

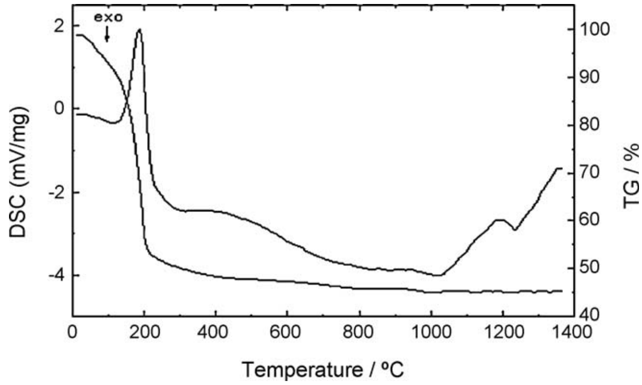

Fig. 2. TG–DTA curves of the as-prepared powder.

into amorphous Al_2O_3, along with an amorphous band at $2\theta \approx 22^\circ$, which is characteristic of amorphous SiO_2. After calcination at 800 °C, the diffraction peaks of Al–Si spinel phase appeared, and on further calcining to 1000 °C and then 1200 °C the Al–Si spinel phase was preserved but with gradually increased intensity. When the heating temperature reached 1250 °C, the diffraction peaks, corresponding to orthorhombic mullite, appeared in the XRD pattern. The lattice parameters of the mullite phase were determined to be $a = 0.7550$ nm, $b = 0.7688$ nm, and $c = 0.2889$ nm, agreeing with the data ($a = 0.7546$ nm, $b = 0.7690$ nm, and $c = 0.2884$ nm) of stoichiometric mullite, as reported in the JCPDS standard card (NO. 15-0776). With all the results considered, the sequence of phase development could be summaried as follows: AACH → AlO(OH) → amorphous Al_2O_3 → Al–Si spinel → orthorhombic mullite. Amorphous SiO_2 was accompanied with the related aluminium species in every stage before the formation of mullite.

3.2. Powder morphology

Fig. 3 shows the TEM photographs of the as-prepared powder and powders calcined at various temperatures. The as-prepared powder containing AACH and amorphous silica is composed of particles showing irregular morphology with a broad size distribution (Fig. 3(a)). The mixed powders of amorphous silica and AlO(OH) exhibit fibrillar or needlelike particles (Fig. 3(b)), and this morphology persists with increasing temperatures up to 1000 °C, at which temperature part of the needlelike particles convert to grained ones with about 10 nm in size (Fig. 3(c)). Literature [14,15] reported that the pre-mullite powders deveried from a mixture of two alkoxides or a mixture of aluminium chloride and tetraethylorthosilicate consist of needlelike particles. The present result agrees with the literature data. The mullite powder formed from the Al–Si spinel and amorphous silica at 1250 °C shows faceted morphology with prismatic plate, and the particle size is about 30–40 nm (Fig. 3(d)). The specific surface area of the mullite powder was determined to be 45.3 $m^2\ g^{-1}$, based on which the average particle size calculated is about 42 nm, corresponding to the result of the TEM observation.

3.3. Densification behavior

Fig. 4 shows the sintering curves of the powders obtained by calcining the azeotropically distilled powders at 800 °C,

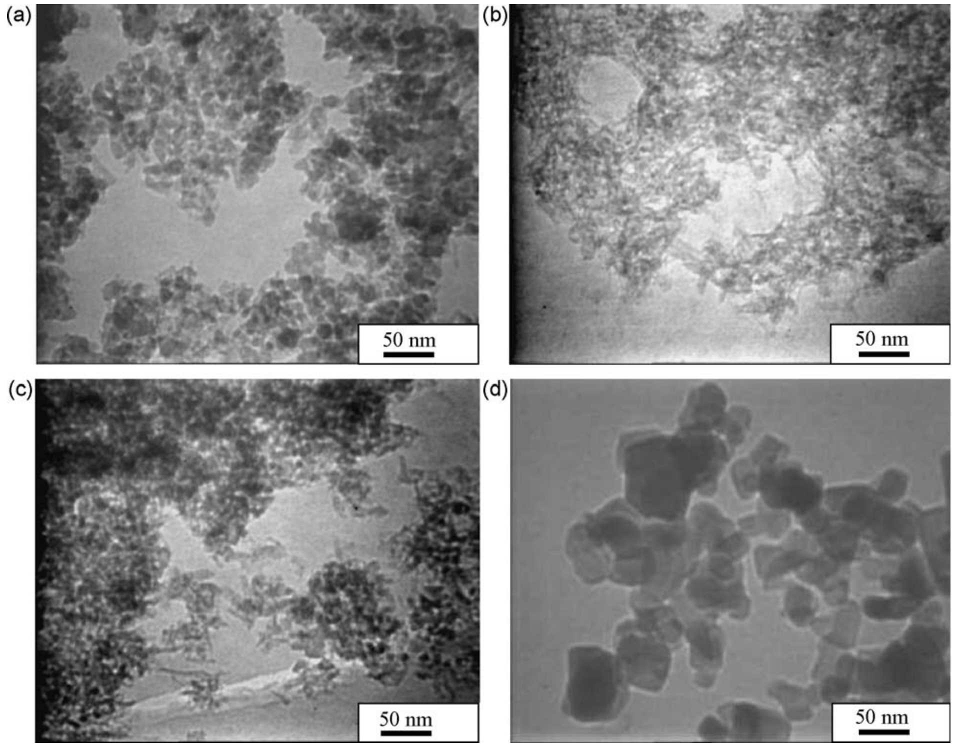

Fig. 3. TEM photographs of the as-prepared powder and powders calcined at different temperatures. (a) As-prepared powder, (b) 200 °C, (c) 1000 °C, and (d) 1250 °C.

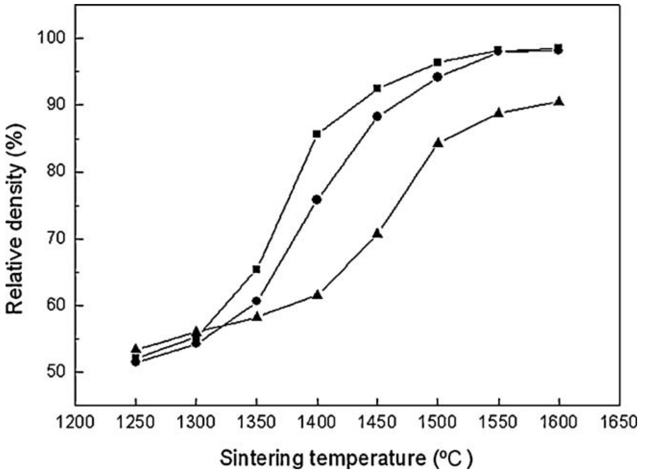

Fig. 4. Change in relative density with sintering temperature for mullite powder (▲) and pre-mullite powders calcined at 800 °C (●) and 1000 °C (■).

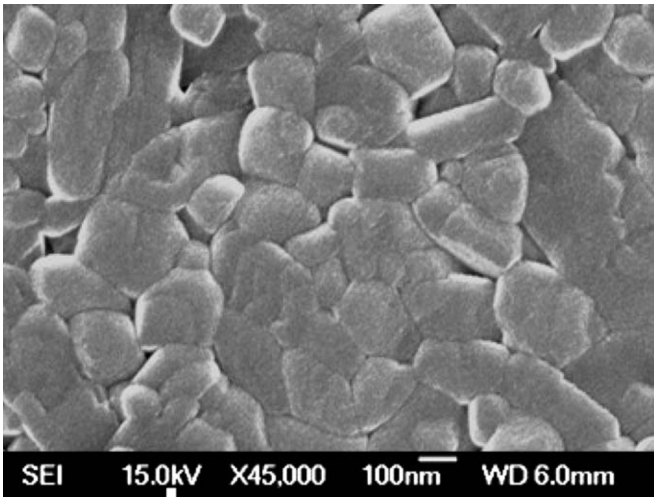

Fig. 5. SEM photograph of polished and thermally etched surface of mullite ceramics sintered at 1550 °C for 2 h.

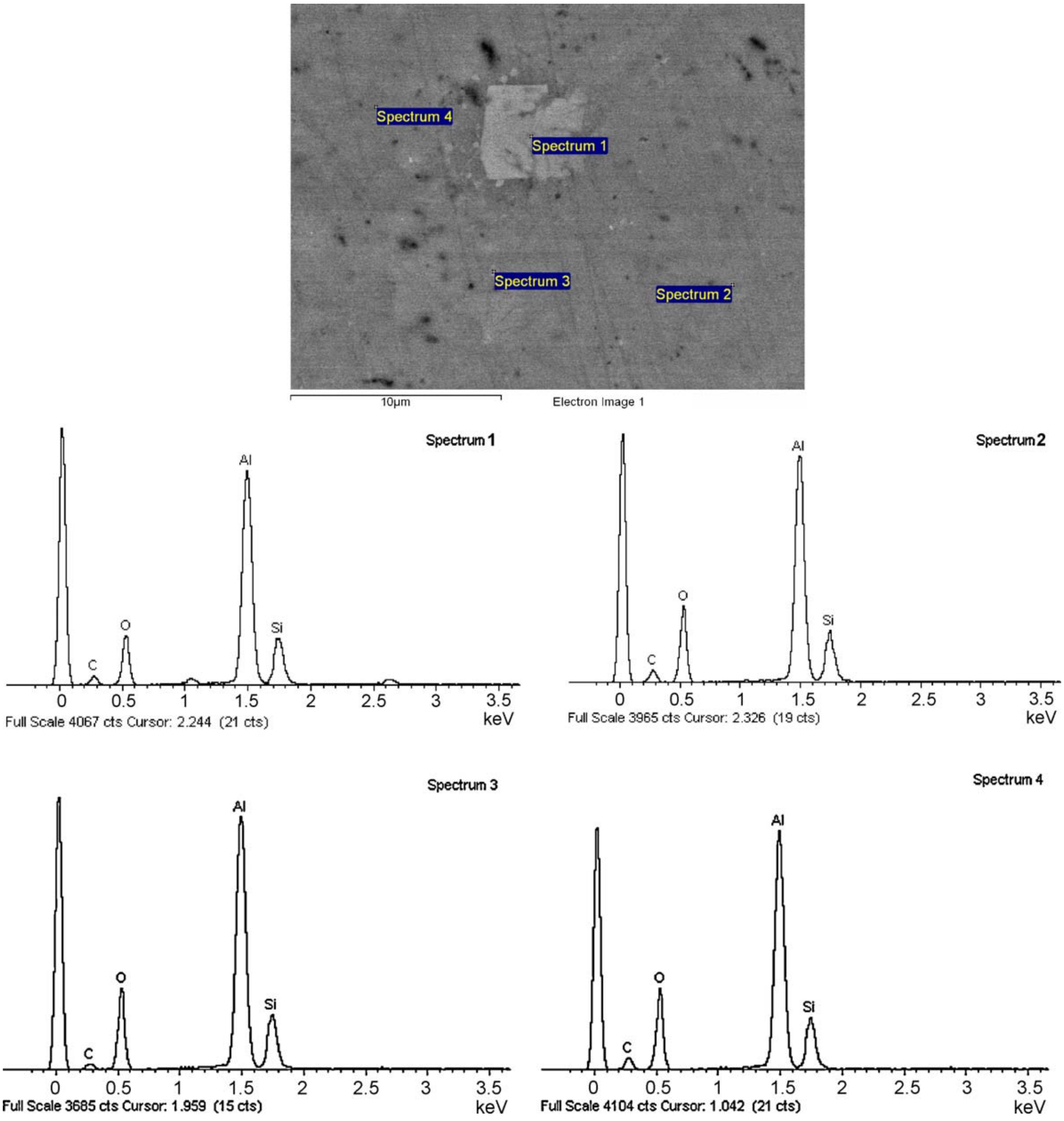

Fig. 6. SEM photograph and EDS analysis patterns of mullite ceramics described in Fig. 5.

1000 °C and 1250 °C, respectively. It can be seen that the powder calcined at 1000 °C shows a lower onset temperature of rapid densification and a higher densification rate. The powders calcined at 800 °C and 1000 °C can be sintered to ≥98% of theoretical density at the temperature of 1550 °C, and with increasing the temperature to 1600 °C the relative density of the sintered compacts can be further increased. In contrast, the 1250 °C calcined powder, which has a crystallized mullite phase structure, sintered to 88.8% and 90.5% of theoretical density at the temperature of 1550 °C and 1600 °C, respectively.

As the mullite formation was almost complete at 1250 °C, the viscous flow of the amorphous phase for densification could not be utilized or could have only a limited effect, and no great densification occurred at the temperatures ≤1300 °C, which is difference from the case for microcomposite particles system [16]. However, as can be seen from Fig. 4 that the powder calcined at 1000 °C can be sintered to 85.5% of theoretical density at the temperature of 1400 °C, while the crystalline mullite powder do not exhibit a great deal of densification up to 1400 °C, which was similar to the results reported by literatures [17,18]. Compared to the crystalline mullite powder, the powder calcined at 1000 °C shows excellent sintering activity and can be sintered to nearly dense mullite body at the temperature of 1550 °C. This sintering temperature is much lower than those required for the formation of dense mullite materials with similar composition [19,20].

Fig. 5 shows the microstructure of the compact derived from the 1000 °C calcined powder and sintered at 1550 °C. The sintered body exhibits a very fine interlocking equiaxed and polygonal grain morphology with grain size in the range of 100–200 nm, and the residue pores are mainly located at the grain boundaries. No elongated grains or glassy phases were formed, which shows that there is little or no liquid phase during sintering, because elongated grains can only grow in the presence of a liquid phase, and the glassy phase may modify the mullite grain morphology from equiaxed to acicular [21,22]. In addition, the chemical uniformity of the prepared powder may also be an important factor in the formation of the nearly equiaxial, fine-grained microstructure during sintering [16].

The selected area EDS analysis results for the compact derived from the 1000 °C calcined powder and sintered at 1550 °C are given in Fig. 6 and Table 1, which show that mullite sintered body obtained has a relatively uniform chemical composition. The Al_2O_3 content is 71.52% on the average and the Al_2O_3/SiO_2 mole ratio is 1.48, which are near the value in the ideal stoichiometric composition of mullite.

Table 1
The contents of Al_2O_3 and SiO_2 in mullite determined by EDS.

Spectrum	Al_2O_3 (wt%)	SiO_2 (wt%)	Total (wt%)
Spectrum 1	71.56	28.44	100.00
Spectrum 2	71.73	28.27	100.00
Spectrum 3	71.32	28.68	100.00
Spectrum 4	71.46	28.54	100.00
Mean	71.52	28.48	100.00

4. Conclusions

Ultrafine pre-mullite powders have been prepared from colloidal silica and aluminium nitrate via carbonate coprecipitation and followed by calcination. The as-prepared precipitation powders are composed of AACH and amorphous silica, which convert to mullite via the Al–Si spinel phase and it is almost complete at 1250 °C. Calcination of the as-prepared powder at 1000 °C gives a very active powder which can be reactively sintered to 98.2% theoretical density at 1550 °C. The sintered body possesses a relatively uniform chemical composition with Al_2O_3/SiO_2 mole ratio of 1.48 and exhibits a very fine interlocking equiaxed and polygonal grain morphology with grain size of 100–200 nm. The high sintered density and fine microstructure of the mullite ceramic obtained in this study are mainly benefited from the good chemical uniformity and ultrafine particle size of the pre-mullite powders.

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