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Synthesis and Characterization of Rich Silica Mullite Fibers by Sol–Gel Method Using Aluminum Lactate and Silica Sol

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Abstract

Rich silica mullite fibers were prepared from an aqueous solution of aluminum lactate and silica sol by the sol–gel method, in which the Al/Si molar ratio of fibers was 0.64. The aluminum lactate was prepared by mixing aluminum nitrate and lactic acid in the molar ratio of 1:3. The fibers sintered at 1200°C presented as an amorphous phase, with a rough surface and uniform diameter. Mullite and silica phases were obtained after the fibers were sintered at 1400°C for 1 h, and the mullite whiskers were observed at the fibers surface, with a high aspect ratio of >10 (about 0.06 μm in diameter). The diameter of the whiskers reached about 0.5 μm at fibers surface when the fibers were sintered at 1600°C for 1 h.

Keywords

Mullite, fibers, whiskers, sol–gel method, aluminum lactate

1. Introduction

Mullite ($3Al_2O_3 \cdot 2SiO_2$) has been recognized as an outstanding ceramic material, for its high temperature strength, creep resistance, thermal and chemical stability, low thermal expansion coefficient and good dielectric properties [1]. In the Al_2O_3–SiO_2 system, only mullite exists as the stable compound, which occupies the structure of edge-shared AlO_6 octahedral chains parallel to the c-axis bounded by an aluminum and/or silicon tetrahedron [2]. Mullite displays various Al to Si ratios according to the solid solution formula $Al_{4+2x}Si_{2-2x}O_{10-x}$, with x ranging between about 0.2 and 0.9 (about 55–90 mol% Al_2O_3) [1]. The compositional variation is based on the exchange of $O^{2-} + 2Si^{4+} \rightarrow 2Al^{3+} + \Upsilon$, which introduces

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one oxygen vacancy [3]. The properties of mullite may be affected by the exchange. Further research continues to define better these correlations.

An important potential application of mullite is its use as fiber reinforcement. The main processes for the manufacture of ceramic fibers can be classified as melt-spinning processes and sol–gel spinning processes [4]. Usually, the melt-spinning method was adopted for the synthesis of ceramic fibers with low melting point, so it was not suitable for the preparation of the mullite fibers.

Many successful processes have been reported for the preparation of mullite fibers by the sol–gel method [5–7]. Amongst the starting materials, most methods use aluminum isopropoxide (AIP) as Al source. However, since the AIP is expensive, its use in the synthesis of mullite fibres is somewhat limited for widespread applications, although the mullite fibres that are obtained have a smooth surface and dense microstructure [4].

The Al_2O_3–SiO_2 system had a lowest melting point when the content of alumina was 9 wt%. The liquid phase could be obtained in the rich silica system at low temperature. The liquid phase could help mullite firing, and mullite fibers with a dense microstructure could be obtained. It is desirable to fabricate the rich silica mullite fibers of high quality using a low-cost Al source.

Recently, rich silica mullite fibers were prepared by sol–gel method using aluminum lactate (AL) and silica sol. The AL was prepared by mixing aluminum nitrate and lactic acid in a water bath (80°C). The content of silica sol added was more than the stoichiometric silica content of mullite, which was in order to detect the effect of silica on fiber microstructure and mullitization. The results indicated that the mullitization of fibers was delayed and mullite whiskers were observed at the fiber surface.

2. Experimental

2.1. Preparation of Samples

The starting materials used were aluminum nitrate (chemically grade, Xi'an reagent factory, Xi'an, China), lactic acid (chemically grade, Xi'an reagent factory, Xi'an, China), silica sol (20 wt% of silica, Shandong Zibo Youjinte Silica Sol Co. Ltd., Shandong, China).

The rich silica mullite fibers were prepared as the processing steps shown in Fig. 1. The aluminum lactate (AL) solution was prepared by mixing H_2O, aluminum nitrate and lactic acid with molar ratio of 30:1:3, followed by heating in a water bath at 80°C. A proper amount of silica sol was added in AL solution to obtain a stoichiometric Al/Si ratio of 0.64. Then, the precursor solution was concentrated to obtain spinning sol in the water bath (80°C), and the sol fibers were prepared by pulling a thin glass rod slowly from the sol after immersing. Afterwards the obtained sol fibers were dried at 60°C for 24 h in an oven. The gel fibers were then sintered at various temperatures between 1000 and 1600°C for 1 h with a heating rate of 1°C /min.

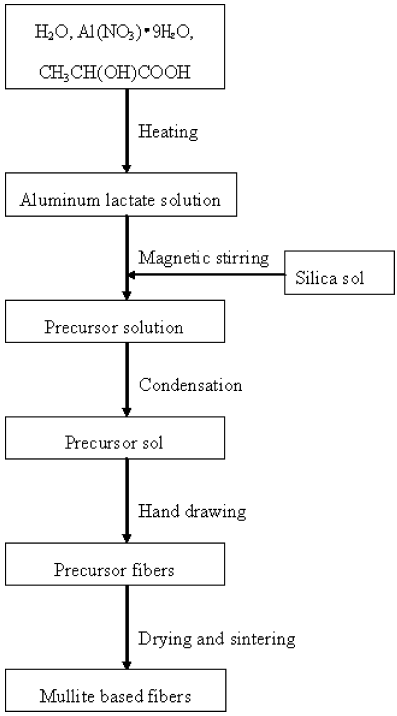


Figure 1. Schematic view of the production route for rich silica mullite fibers.

2.2. *Characterization*

For the gel, the thermal behavior was measured by TG/DSC instruments (SDT Q600, TA Instrument, American) at a heating rate of 10°C/min in flowing air, and Fourier transform infrared (FTIR) spectra were recorded on a 6700 Infrared Spectrometer (Nicolet Magna, American) with the samples as KBr pellets. X-ray diffraction analysis was carried out on a DX-2500 X-ray Diffractometer (Dandong Fangyuan, Dandong, China) using CuKα radiation, with a step width of 0.05°/s. Morphologies of heat-treated fibers were characterized by scanning electron microscopy (JSM-6390LV, JEOL, Japan). All tests were done at room temperature.

3. Results and Discussion

Aluminum lactate was prepared by the reaction between aluminum nitrate and lactic acid in aqueous solution, with constant stirring and heating. The main chemical reactions can be simplified by the following equations (1) and (2), though the actual reactions were complex:

$$3CH_3CH(OH)COOH + Al(NO_3)_3 \rightarrow Al[CH_3CH(OH)COO]_3 + 3HNO_3, \quad (1)$$

$$HNO_3 \rightarrow 1/2H_2O + 1/4O_2\uparrow + NO_2\uparrow. \quad (2)$$

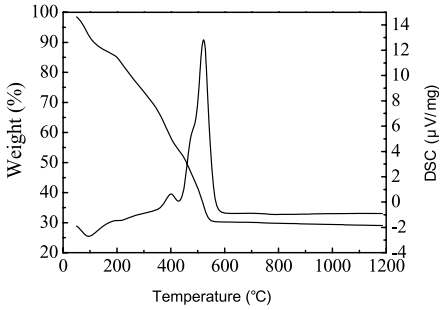


Figure 2. TG and DSC curves of precursor gel fibers.

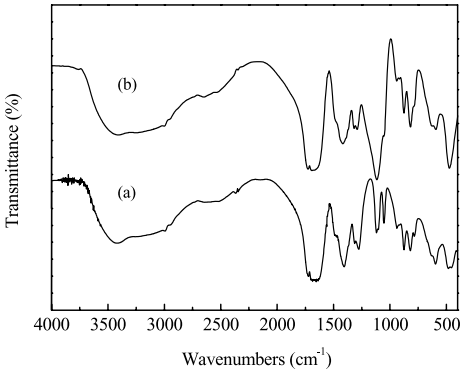


Figure 3. FT-IR spectra of (a) the AL gel and (b) the precursor gel fibers.

The TG/DSC curves of the precursor gel fibers obtained with a heating rate of 10°C/min are shown in Fig. 2. The DSC curve of the gel fibers exhibited an endothermic peak at about 100°C, and two exothermic peaks at about 400°C and 500°C. The endothermic peak is assigned to dehydration of the residual water and decomposition of hydroxides in the gel fibers, whereas the two exothermic peaks are assigned to decomposition of nitrates and the organic component [4], respectively. The TG curve of the gel fibers showed a weight loss of around 70 wt% at 600°C, while almost no further weight loss appeared with increasing temperature.

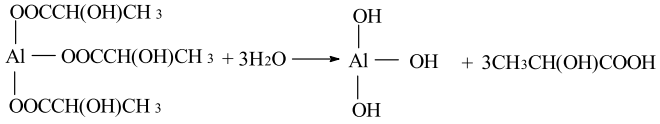
Usually, an exothermic peak was observed by the sol–gel method in the temperature range of 900–1000°C, because the formation of mullite started [4, 5, 7] when the Al/Si ratio in the precursor gel was 3:1. But, in the present work, the exothermic peak was not observed until 1200°C, and the formation of mullite did not start beforehand.

The FTIR spectra of AL gel and precursor gel fibers are shown in Fig. 3. As can be seen, the bands at 3410 and 1120 cm^{-1} are assigned to the O–H stretching modes and bending modes of adhesive and constitution water as well as lactic acid OH, respectively. The band at 2650 cm^{-1} maybe be assigned to the O–N stretching mode of nitric acid. The bands at 1680 and 480 cm^{-1} are assigned to the C=O stretching mode and bending mode, respectively. The band at 940 cm^{-1} is assigned

to the C–C stretching mode. The bands at 1300 and 880 cm^{-1} may be assigned to the C–O stretching mode and bending mode, respectively. As can be seen, a little nitric acid and some lactic acid were present in the samples.

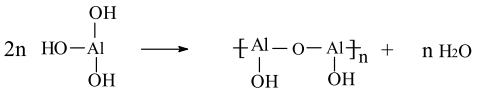
The AL gel was obtained by condensation of AL solution in the water bath (80°C). As shown in Fig. 3(a), the band observed at 1420 cm^{-1} corresponds to Al–OH bonding mode [8]. The stretching modes of Al–O–Al linkages are observed at 620 and 816 cm^{-1} [9]. When the AL solution was condensed, hydrolysis, condensation and polycondensation could occur, and some lactic acid could evaporate, which caused the reaction to proceed in the right direction [10–12]. So, the stretching modes of Al–O–Al linkages are observed. The mainly reactions can be simplified as the following equations (3) and (4):

Hydrolysis:



(3)

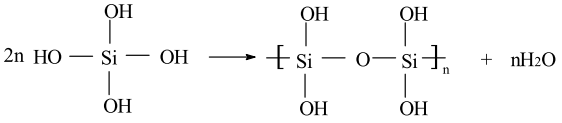
Condensation polymerization:



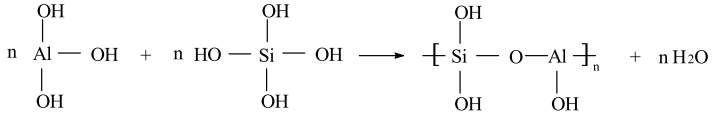
(4)

As shown in Fig. 3(b), the bands at 1050 and 478 cm^{-1} are assigned to the stretching and bending modes of Si–O–Si of the network. The band at 620 cm^{-1} has a shoulder at 705 cm^{-1}, which may be assigned to the (Si, Al)–O–(Si, Al) linkages bending mode [13].

The condensation polymerization of silica sol also took place when the sol was concentrated. The main reactions can be simplified as the equations (5) and (6). The condensation polymerization reaction between aluminum and silicon hydroxide occurred simultaneously according to equation (6) [7].



(5)



(6)

After the concentrating process in the water bath at 80°C, a spinnable sol was obtained, for the linear molecular chains were present.

The X-ray diffraction patterns of precursor gel fibers sintered at 1000, 1200 and 1400°C are shown in Fig. 4. The main phase was amorphous in the samples after being sintered at 1000 and 1200°C, with few Al–Si spinel generated. Mullite

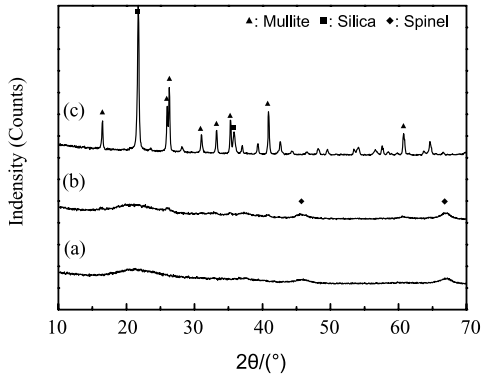


Figure 4. XRD patterns of the precursor fibers heated at (a) 1000, (b) 1200 and (c) 1400°C for 1 h.

and silica phases were obtained after being sintered at 1400°C, and the content of mullite was about 77% according to calculation of the diffraction peak intensity.

Usually, the formation of mullite by sol–gel methods starts at 1000°C and no other phase remains in the samples after full reaction. Usually, the formation of mullite by sol–gel methods starts at 1000°C and no other phase remains in the samples after full reaction [4]. The formation of the mullite nucleation sites (AlO_5 sites) closes to 1000°C; moreover, the further densification by the growth of particles and clusters exceeds the critical size of mullite nuclei, which results in rapid mullitization with a very high nucleation density [14]. But the spinel phase was obtained in the samples because organic acids induced silica-alumina micro-phase separation, which could generate the formation of AlO_4 units. Moreover, trapping of residual isolated –OH groups had been found in the structures after the structural breakdown at slow heating rate. The formation of the spinel phase from the AlO_4 units and residual –OH groups decreased the possibility of occurrence of the intermediate phase [15].

Furthermore, the full mullitization of fibers was delayed until 1400°C because the content of silica sol added was more than the stoichiometric silica content of mullite. It has been accepted that mullite formation in reaction sintering couples of quartz and Al_2O_3 is controlled by dissolution precipitation reactions, where Al_2O_3 species dissolve in the coexisting SiO_2 liquid until a critical Al_2O_3 concentration is reached [16]. It was difficult for mullite nucleation to form through alumina dissolution and diffusion at low temperature. Therefore, the mullite phase was obtained until 1400°C.

SEM micrographs of precursor fibers sintered at 1200°C for 1 h are shown in Fig. 5. The fibers had a diameter ranging from 10 to 30 μm, with a rough surface and uniform diameter. The fibers of rough surface were obtained because the aluminum lactate had a high decomposition temperature [17].

SEM micrographs of mullite fibers sintered at 1400°C for 1 h are shown in Fig. 6. The mullite whiskers were observed at fiber surfaces, with a high aspect ratio of >10 (about 0.06 μm in diameter). A little of the liquid phase could also be present

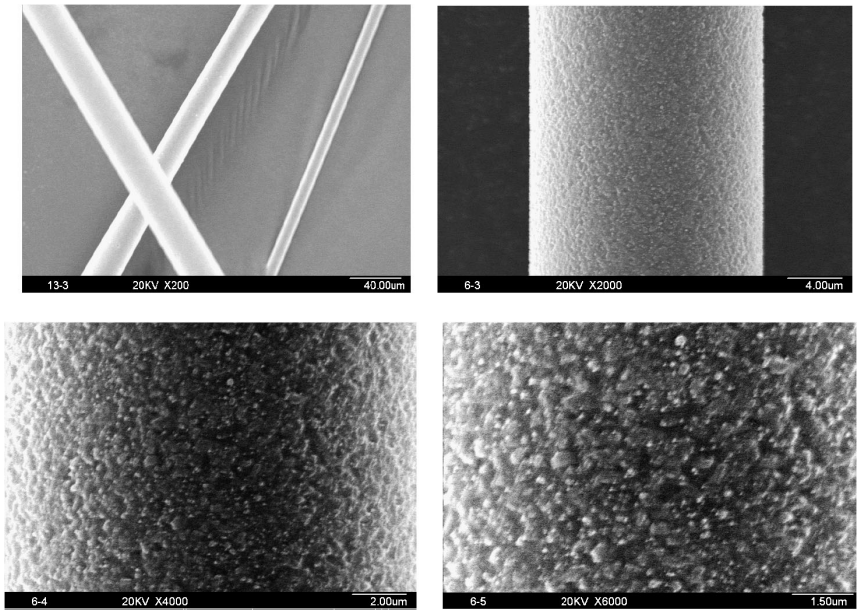


Figure 5. SEM microstructures of the precursor fibers heated at 1200°C for 1 h.

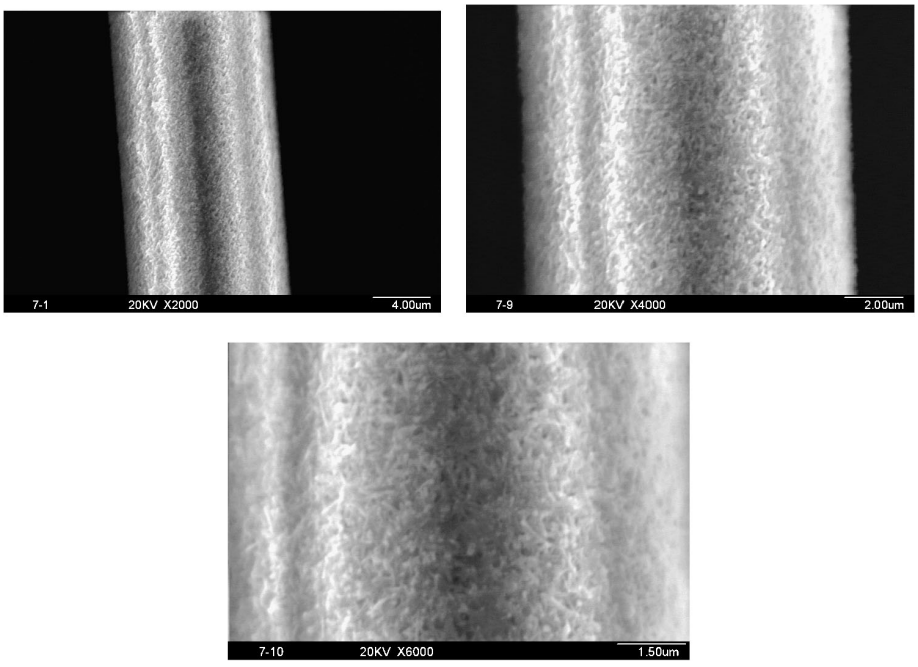


Figure 6. SEM microstructures of the precursor fibers heated at 1400°C for 1 h.

in the Al_2O_3–SiO_2 system at 1400°C, for alumina and silica particles were in the nanometer size range. Otherwise, some Na^+ may be present in the silica sol, which

helped formation of low melting point liquids. Mullite grains have a strong tendency towards anisotropic growth as the grain growth is underway in an unconstrained environment [18]. Selective precipitation was occurring at the crystal faces at the tip of the whisker whilst the longer planar surfaces of the whisker grew at a slower rate.

The whiskers were observed without being etched by HF solution, because the liquid phase moved to the fiber center when the fiber temperature decreased, and this exposed the whiskers.

SEM micrographs of precursor fibers sintered at 1600°C for 1 h are shown in Fig. 7. The mullite whiskers also were observed, with a high aspect ratio of >10 (about 0.5 μm in diameter). The enhanced volume fraction and the decreased viscosity of liquid phase at 1600°C were advantageous to whisker growth. A dense microstructure was obtained inside the fibers.

The EDS spectrum of the whiskers on the fiber surface is shown in Fig. 8(a), which contained 55.08 wt% Al_2O_3 and 44.92 wt% SiO_2 (Al/Si = 0.72, molar ratio). This result indicated an alumina composition stoichiometrically deficient with respect to mullite (Al/Si = 3, molar ratio). Mullite displays variable aluminum/silicon ratios within the solid solution series $Al_{4+2x}Si_{2-2x}O_{10-x}$, with x ranging between about 0.2 and 0.9 (corresponding to about 55–90 mol% Al_2O_3), and the various types of mullites formed depended on the synthesis processes [1]. A 0.64 molar ratio of Al/Si was stoichiometrically deficient to that of the mullite in the samples, and this resulted in whisker composition that deviated from the stoichiometry.

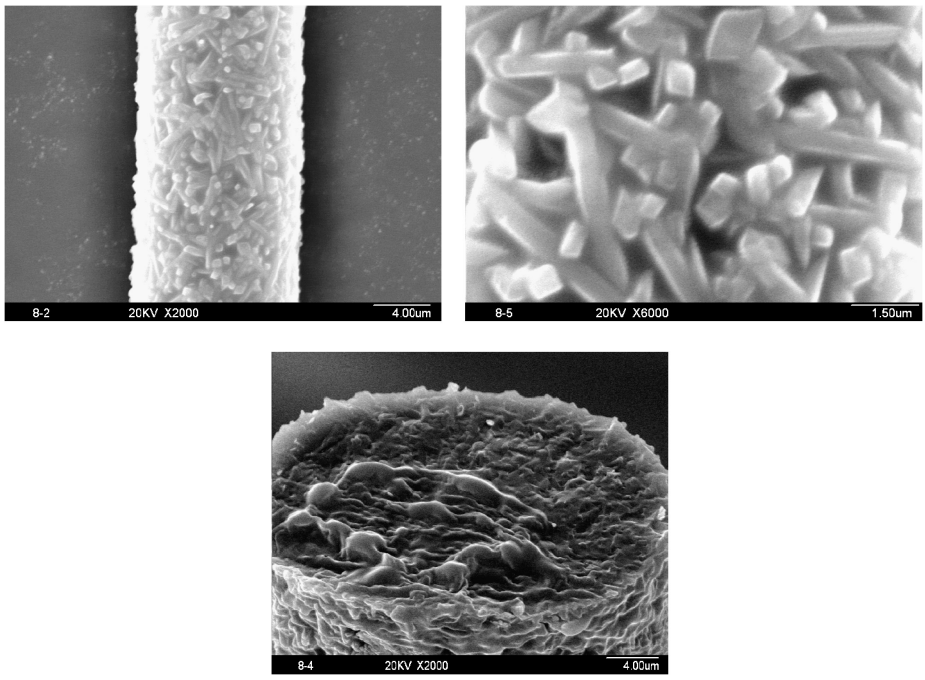


Figure 7. SEM microstructures of the precursor fibers heated at 1600°C for 1 h.

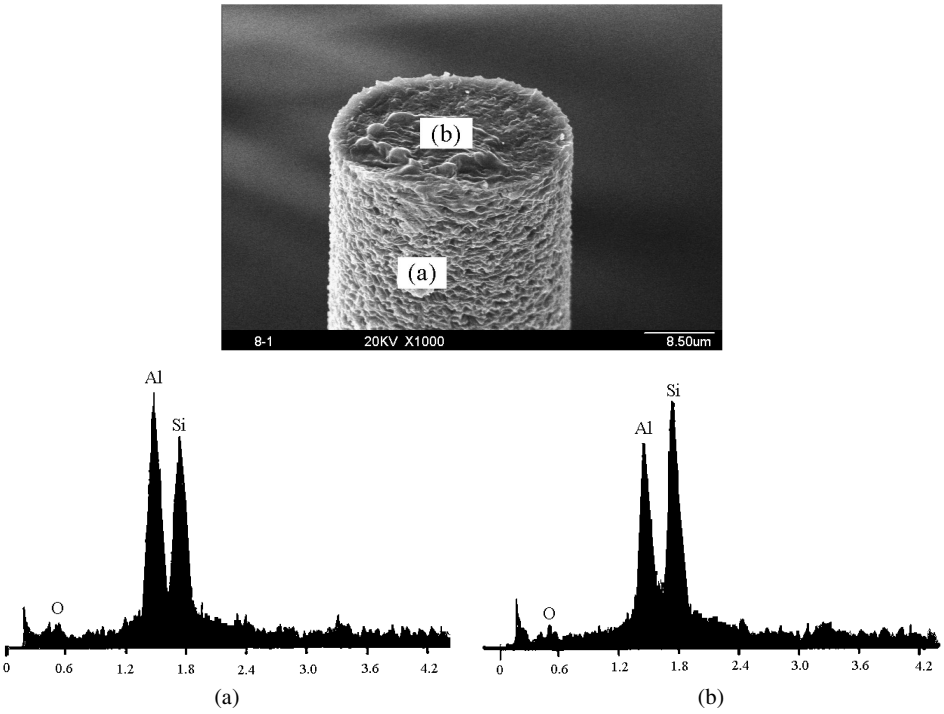


Figure 8. The EDS spectrum of (a) the whiskers of fibers surface, this showing ion concentration (wt%) of 11.69 O, 36.15 Al and 52.16 Si; and (b) the cross-section of fibers, this showing ion concentration (wt%) of 7.46 O, 30.71 Al and 61.83 Si; which the precursor fibers were heated at 1600°C for 1 h.

The EDS analysis was also influenced by the background materials which could have been derived from material other than the whiskers.

The EDS spectrum of the cross-section of fibers is shown in Fig. 8(b), from which we can conclude that the cross-section contained 46.78 wt% Al_2O_3 and 53.22 wt% SiO_2 (Al/Si = 0.52, molar ratio), and this result indicated silica and mullite coexisting inside the fibers.

4. Conclusion

Rich silica mullite fibers were prepared using AL solution and silica sol. The AL solution was obtained from the reaction of aluminum nitrate with lactic acid in a molar ratio of 1:3. The mullitization of fibers would be delayed if the content of silica sol added was more than the stoichiometric silica content of mullite. Amorphous fibers with a rough surface and uniform diameter were obtained after sintering at 1200°C for 1 h. Mullite and silica phases were obtained by sintering at 1400°C for 1 h, and the mullite whiskers were observed at fiber surfaces, with a high aspect ratio of >10 (about 0.06 μm in diameter). The whisker diameter reached about 0.5 μm at the fiber surface when the precursor fibers were sintered at 1600°C for 1 h.

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