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Preparation and characterization of mullite whiskers from silica fume by using a low temperature molten salt method

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ABSTRACT

Mullite whiskers were prepared from silica fume in molten $Al_2(SO_4)_3$–Na_2SO_4 mixture salts at low temperatures. The resulting mullite whiskers, as well as the nucleation and growth mechanism in the molten environment, have been investigated by using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and thermogravimetric analysis (TG–DTA) techniques. XRD studies showed that the materials obtained were orthorhombic mullite. SEM, TEM and HRTEM results revealed that the mullite whiskers were single crystal fibers with diameters ranging from 30 to 150 nm and lengths of over several microns. According to thermodynamic analysis, mullite phase might be spontaneously formed in molten salts as the temperature reached the decomposition temperature of aluminum sulfate (1023 K). Moreover, the mullite crystals grew along [1 1 1] crystal plane firstly and developed into fibrous microstructure finally.

1. Introduction

Mullite has been recognized as an important material for high-temperature structural applications due to its good mechanical strength, excellent thermal shock, high creep resistance, a low thermal coefficient of expansion, and good dielectric properties. Mullite whiskers are effective materials for the reinforcement of various composite materials because of their high strength and stiffness combined with large aspect ratios. Many efforts have made to prepare mullite whiskers, including thermal decomposition of minerals [1], rare earth oxide doping [2,3], sol–gel pressing [4], internal crystallization method [5] and high-energy ball milling process [6–9]. However, mullite formation by conventional methods requires a temperature of above 1200 °C, and full crystallization occurs at around 1600 °C. Developing new approaches to prepare mullite whiskers at lower temperature still remains a challenge. Molten salt synthesis has been employed to synthesize various ceramic powders because it requires low reaction temperature and gives powders with homogeneous morphology. Molten salts provide liquid environment in which the growth of whiskers is easily facilitated. Nucleation and growth of grains are dependent on dissolution of chemical reagents in the molten flux. A number of studies have been reported on the preparation of mullite whiskers by using molten salt synthesis. Zhang et al. synthesized mullite whiskers from various alumina and silica sources in Na_2SO_4 flux [10,11]. Ouatib et al. prepared mullite whiskers through the reaction of aluminum sulfate and amorphous silica in molten eutectic $(Na_{0.8}K_{0.2})_2SO_4$ [12]. Tan synthesized mullite whiskers from coal fly ash using sodium sulfate flux [13]. Park et al. obtained orthorhombic mullite whiskers with a diameter of 0.6–1.8 μm by firing compacts of coal fly ash and $NH_4Al(SO_4)_2\cdot 12H_2O$ powders [14]. However, all these methods required temperatures of >900 °C to form.

Silica fume emerges as a by-product from the melting ferrosilicon alloy. This industrial waste presents serious problems of storing and environmental pollution. Therefore, the effective utilization of waste silica fume not only decreases environmental pollution, but also produces high value-added products. Grace et al. prepared mullite ceramics from fumed silica and various aluminas [15] through sintering the mixture powders, and the final sintering temperature was 1550 °C. Yugeswaran et al. synthesized mullite ceramic from coal ash by using transferred arc plasma processing (TAP) technique [16]. Li et al. prepared self-reinforcement mullite ceramics through in situ synthesis of mullite whisker in flyash body [17]. To the best of our knowledge, there is no report on preparation of mullite whiskers using silica fume as SiO_2 source via low temperature molten salt method. We synthesized mullite whiskers through the reaction of aluminum sulfate and silica fume in sodium sulfate at temperatures ranging from 750 to 900 °C. Mullitization occurred at a temperature of as low as 800 °C, which is the lowest temperature for mullite whisker formation via molten salt method.

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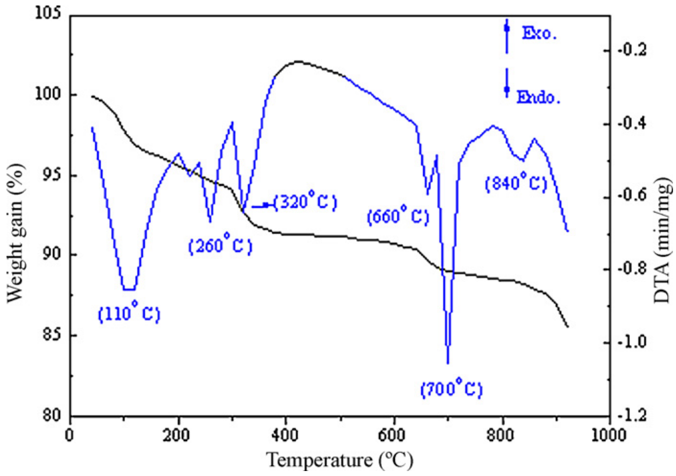

Fig. 1. TG and DTA curves of the mixture.

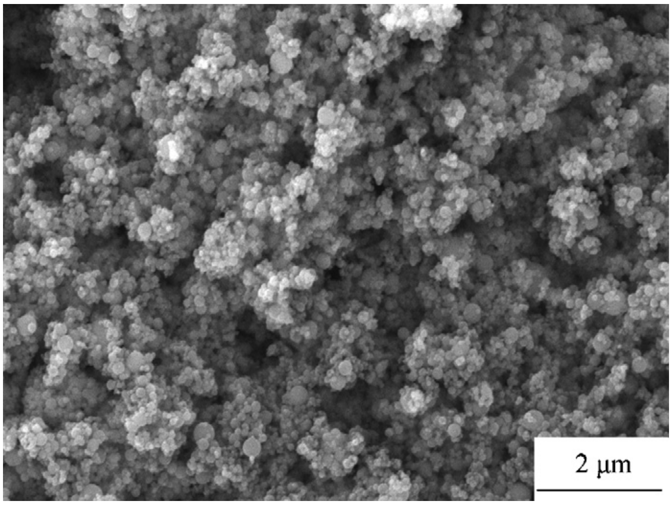

Fig. 2. SEM image of the silica fume.

2. Experimental procedures

As raw materials, aluminum sulfate hydrate [$Al_2(SO_4)_3 \cdot 18H_2O$, AR], sodium sulfate [$Na_2SO_4$, AR] and ethanol (AR) (Xi'an Chemical Reagent factory) were used. Silica fume ($SiO_2 > 99\%$, Xi'an Linyuan Silica Fume Ltd.) was industrial product.

Aluminum sulfate hydrate was placed in a microwave oven and heated with high fire for 10 min to remove intra-molecular crystal water. Then, aluminum sulfate and the silica fume were weighed accurately in order to control Al/Si molar ratio to be 3:1. The weight of sodium sulfate was equal to the total weight of aluminum sulfate and silica fume. The mixture was grinded in a ceramic mortar for 30 min, and then heated at a rate of 300 °C/h to final temperatures of 700 °C, 750 °C, 800 °C and 900 °C for 1 h. The samples were washed with 95 °C water to remove the sulfate. Finally, white mullite powders were obtained after filtration, washing and drying. Crystalline phase and morphology of the powders were examined by using X-ray diffractometer (XRD, D/MAX-RA) and scanning electronic microscope (SEM, S-2700), respectively. Microstructure of the mullite whiskers was observed by using transmission electron microscope (TEM, JEOL-2100F). Thermal analysis (DTA) and thermo gravimetric analysis (TG) were performed by using Netzsch STA 409C thermal analyzer.

3. Results and discussion

TG and DTA curves of the starting mixture (aluminum sulfate, silica fume and sodium sulfate) are shown in Fig. 1. It can be seen that weight loss taking place in following four ranges. The first small weight loss (about 3%) was attributed to the dissociation of absorbed water at 100 °C, with an endothermic peak appearing on DTA curve simultaneously. The second weight loss range resulted from the crystal water of aluminum sulfate occurs between 250 °C and 330 °C, corresponding to two endothermic peaks at 260 °C and 320 °C. The third weight loss occurs between 650 °C and 710 °C, together with two endothermic peaks, is related to the low-melting point of Na_2SO_4–$Al_2(SO_4)_3$ and the decomposition of $Al_2(SO_4)_3$ above 700 °C [11]. The last weight loss occurs at 860 °C, and there is broad endothermic peak (from 800 °C to 850 °C) on the DTA curve, which indicates the formation of mullite. The broad endothermic peak in our experiment is similar to that reported in Ref. [10]. One a slight difference in peak position is observed, which could be due to the fact that our silica fume is in nanometer scale.

Fig. 2 shows typical SEM images of the silica fume that was generated from rapid oxidation of Si gas in the smelting ferrosilicon alloy industry. It can be seen that the fine silica fume is approximately spherical particle with a mean diameter of 0.3 μm.

Fig. 3 shows phase compositions of the samples obtained at 750 °C, 800 °C, 850 °C and 900 °C for 1 h. Mullite phase has been formed in the sample fired 800 °C. However, diffraction peaks of mullite phase are not found in the sample obtained at 750 °C, and the XRD patterns are not attributed to any determined materials. The broad peak centered at about 22.07° in the samples fired at lower temperatures (750 °C and 800 °C) suggest that silica is amorphous [11].

SEM photographs of the samples are shown in Fig. 4. It can be seen that microstructure of the resultant mullite materials have great difference when prepared at temperatures. Mullite whiskers can be observed in the sample fired at 800 °C (Fig. 4b), however, there is no mullite crystalline phase formed at 750 °C (Fig. 4a). Dimension of the mullite whiskers increases with increasing temperature (Fig. 4b–d). The whiskers possess nanometer-sized diameters and micrometer-sized lengths.

Fig. 5 shows TEM image, HRTEM image and SAED pattern of the 900 °C sample. It can be seen that average diameter of the mullite whiskers is in the range of 30–150 nm and length is over several microns. The selected-area electron diffraction patterns from the

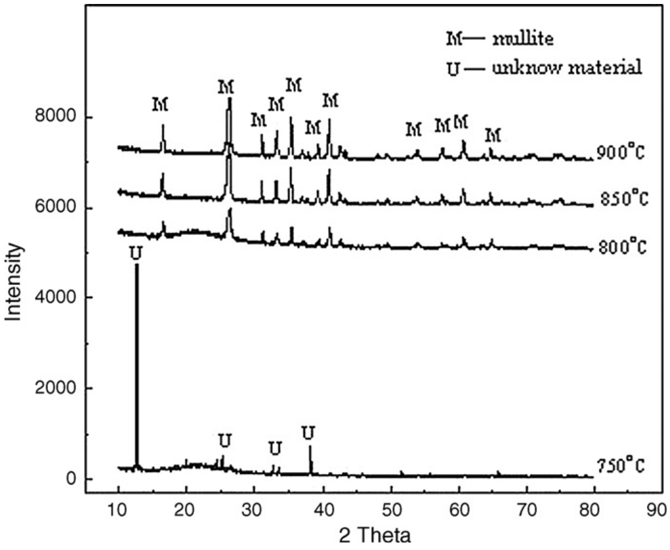

Fig. 3. XRD patterns of the samples prepared at different temperatures.

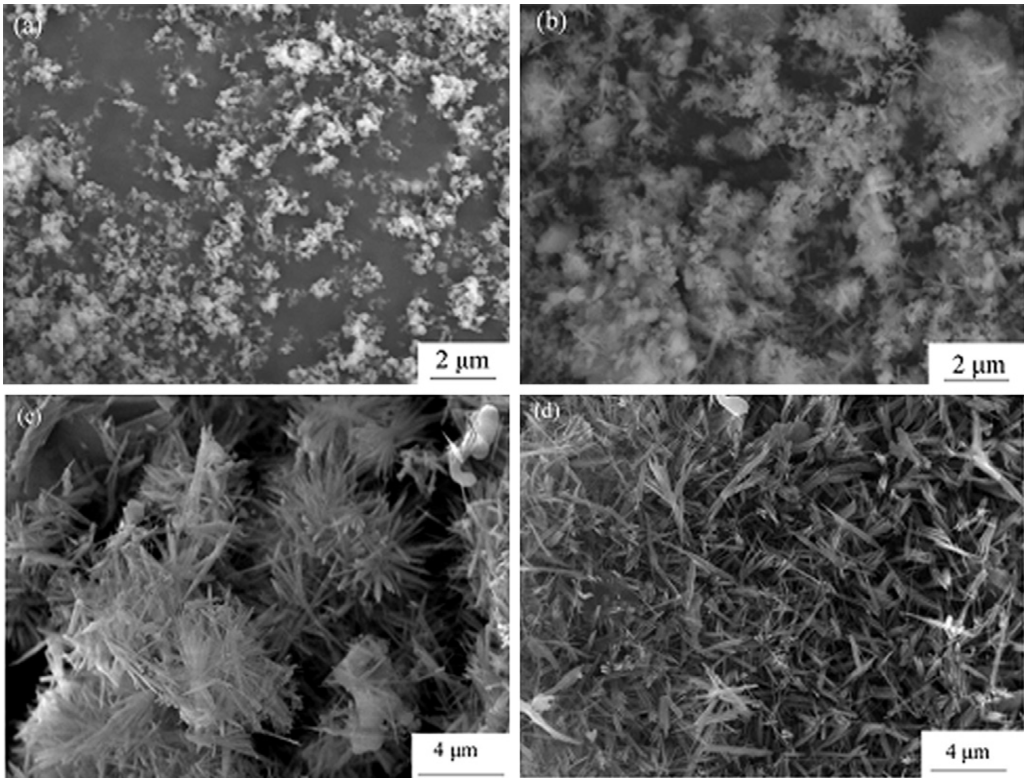

Fig. 4. SEM micrographs of the samples obtained at different temperatures (a, 750 °C; b, 800 °C; c, 850 °C and d, 900 °C).

mullite whisker in Fig. 5(a) can be indexed to the orthorhombic structure. HRTEM image shows that the spacing is 0.254 nm, in accordance with [1 1 1] crystal plane spacing of mullite, which indicates that the mullite crystal grew along [1 1 1] crystal plane firstly and developed into fibrous microstructure finally in the molten salts.

The reaction between silica fume and aluminum sulfate to form mullite can be described as follows.

$$Al_2(SO_4)_3 \rightarrow \gamma\text{-}Al_2O_3 + 3SO_3 \quad (1)$$

$$3\gamma\text{-}Al_2O_3 + 2SiO_2 \rightarrow 3Al_2O_3 \cdot 2SiO_2\,(\text{mullite}) \quad (2)$$

In fact, free cations and anions formed when electrolyte is fired above melting point. According to this principle, free Al-cations firstly formed in the liquid before decomposition of $Al_2(SO_4)_3$, which transformed to amorphous γ-Al_2O_3 above 700 °C. In a second step, the γ-Al_2O_3 subsequently reacted with silica fume according to reaction (2). These yield mullite muclei heterogeneously through Eq. (2), which is a commonly accepted mechanism of mullite formation. However, there is no clear explanation for the two-step reaction mechanism in the open literature from thermodynamic point of view. Thus, we calculated the effect of temperature on free energy change of reactions (1) and (2), which are shown in Fig. 6. The data of G are obtained from Ref. [18]. As far as chemical equilibrium is concerned, the smaller the value of ΔG, the larger is the

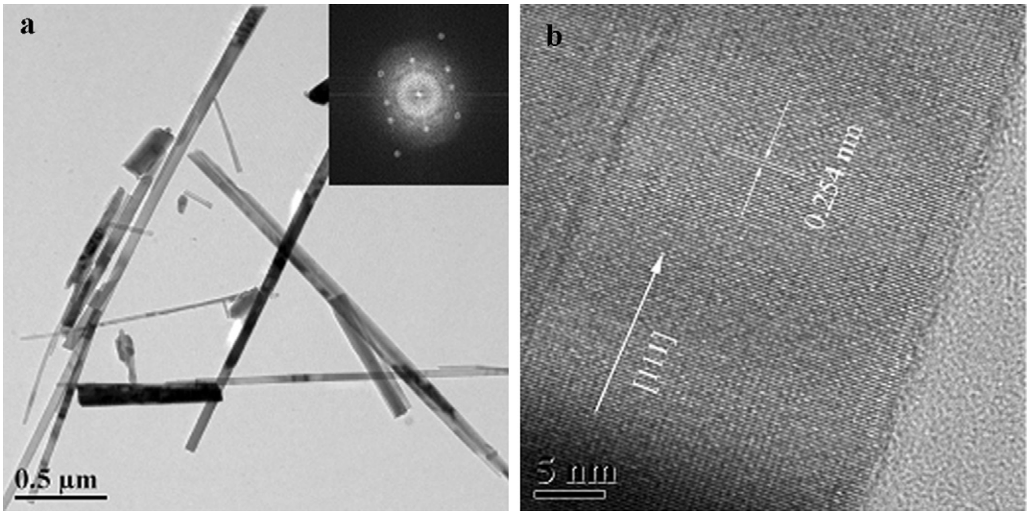

Fig. 5. TEM image and HRTEM image of mullite whiskers in the 900 °C sample. (a) TEM image of individual whiskers after ultrasonic treatment. Inset shows the corresponding SAED pattern of the sample shown in (a). (b) HRTEM image of mullite whisker.

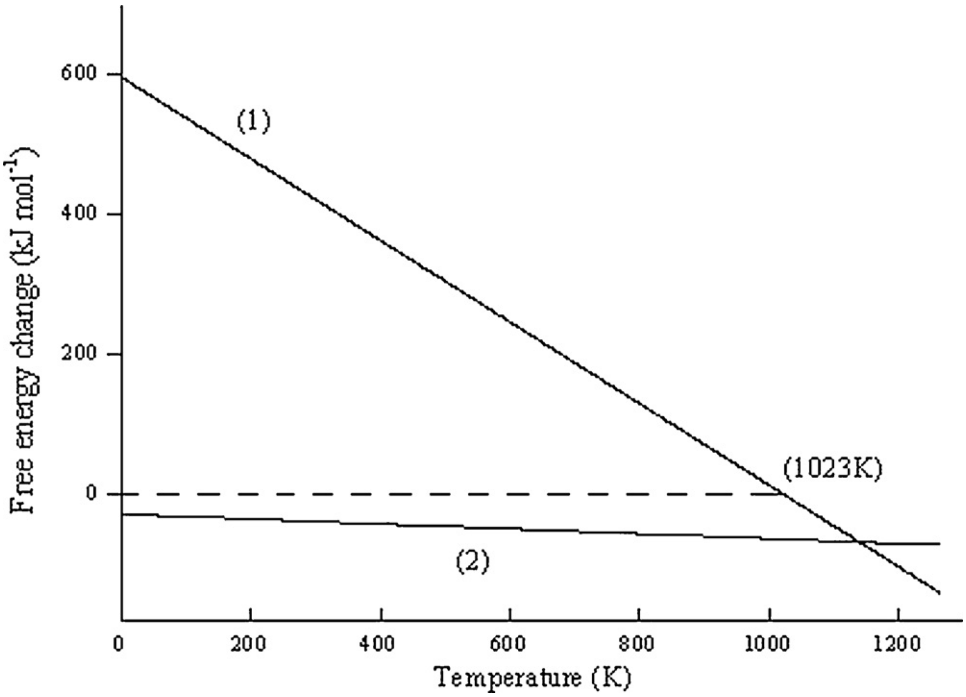

Fig. 6. Change of free energy ΔG for reactions (1) and (2) depending on temperature.

equilibrium constant k, and the more the products are when equilibrium state is attained. Therefore, the reaction (1) cannot process in the lower temperature range ($\Delta G > 0$), the reaction would start extremely vigorously when the temperature was reaching 1023 K ($\Delta G < 0$). It is found that the free energy change of reaction (2) is negative in the whole temperature range, which indicated that this reaction is a spontaneous reaction. From the thermodynamic data of reactions (1) and (2) in the temperature range of 0–1300 K, mullite whiskers form and grow controlled by reaction (1). This implies that mullite phase may spontaneously form once the temperature of the molten salts reaches the decomposition temperature of aluminum sulfate.

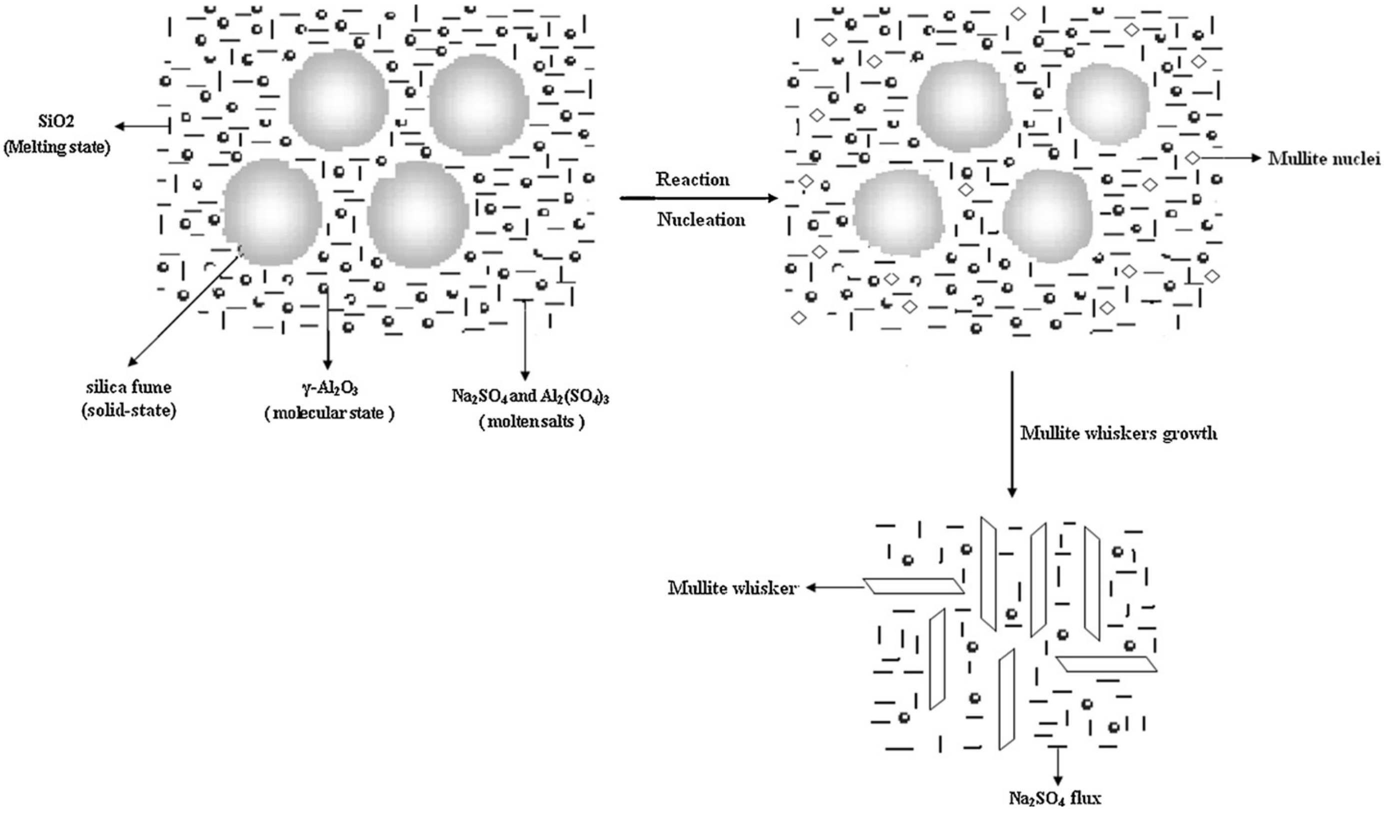

Fig. 7. Schematic illustration of nucleation and growth process of the mullite whiskers.

In the $Al_2(SO_4)_3$–Na_2SO_4 molten salts, aluminum sulfate decomposition and transformation into γ-Al_2O_3 determine the growth rate of mullite whiskers. A schematic illustration is shown in Fig. 7 to describe the growth of mullite whiskers at different stages in the samples. Firstly, free-state γ-Al_2O_3 was formed and silica fume was dissolved in the molten salts simultaneously. Subsequently, homogeneous nucleation occurred in melt due to the reaction of γ-Al_2O_3 and SiO_2. Then, the crystal grew continuously along the [1 1 1] crystal plane of mullite, and longer mullite whiskers were obtained at the end of this stage. The silica fume was consumed continuously in accordance with the following dissolution equilibrium and reaction.

$$\text{Silica fume (s)} \rightarrow \text{silica (l)} \rightarrow \text{mullite (s)}$$

By repeating this dissolution–reaction cycle, the active silica fume was converted into inert mullite phase in the molten salts. Moreover, synthesis of mullite whiskers by this molten salt method is advantageous due to the fact that the reactants are mixed at a molecular level, ensuring chemical homogeneity and thus a lower reaction temperature.

4. Conclusions

Mullite whiskers were prepared from silica fume in molten $Al_2(SO_4)_3$–Na_2SO_4 salts for 1 h at 800 °C, 850 °C and 900 °C. SEM, TEM and HRTEM studies showed that average diameter of the mullite whiskers was in the range of 30–150 nm and their length was over several micrometers. Moreover, mullite crystal grew along the [1 1 1] crystal plane continuously and developed into fibrous microstructure finally. Free energy change of the reaction was calculated. Thermodynamic data indicated that mullite phase may be spontaneously formed as the temperature reached the decomposition temperature of aluminum sulfate (1023 K).

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