Large-Scale Synthesis of Mullite Nanowires by Molten Salt Method

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Single-crystalline mullite (3Al2O3 · 2SiO2) nanowires have been produced in large quantities by a low cost and environmentally benign molten salt synthesis (MSS) method. The raw materials, Al2(SO4)3 and SiO2 powders, react in molten Na2SO4 at 1000 °C to produce mullite nanowires without the use of surfactants or templates. After the synthesis, the remaining salts can be easily separated from the products by washing with water. The final products are characterized by X-ray powder diffraction, field emission scanning electron microscopy, transmission electron microscopy, energy-dispersive X-ray spectroscopy, selected-area electron diffraction, and inductively coupled plasma-atomic emission spectrometry. The thermal and chemical behavior of the raw materials is investigated by heating at a rate of 10 °C/min up to 1200 °C in air followed by thermogravimetric and differential scanning calorimetry analyses. The single-crystalline mullite nanowires have diameters of 30–80 nm and lengths from several hundreds of nanometers to micrometers and the growth mechanism is discussed.

Keywords: Mullite Nanowires, Molten Salt Synthesis, Structure Characterization, TG-DSC, Growth Mechanism.

1. INTRODUCTION

One-dimensional nanostructures such as nanotubes and nanowires have attracted much interest due to the novel structures, quantum confinement effects, unusual properties, and many potential applications.1–4 Mullite (3Al2O3 · 2SiO2) is a superior engineering ceramic material possessing good chemical stability, low thermal expansion coefficient, high deformation resistance at high temperature, and low fracture toughness.5 Together with favorable properties such as excellent creep resistance as well as low dielectric constant and dielectric loss, mullite is widely used as functional ceramic materials in electronics, optics and high-temperature applications.6–8 Micro-sized mullite whiskers, as a good reinforcement material in ceramic-matrix composite, have been fabricated and extensively investigated.9–15 Recent studies have shown that nanoscale whiskers such as nanowires or nanorods have better mechanical properties than their microscale counterparts.16–18 Thus, mullite nanowires or nanorods are good composite reinforcements that could find important applications in functional ceramics due to their high strength and toughness. Although mullite nanowires19,20 nanocolumns21 and nanobelts8 have been reported, large scale synthesis of mullite nanowires by means of a simple, low cost, and environmentally friendly method is challenging thereby stifling wider applications of mullite nanowires.

Recently, molten salt synthesis (MSS) has attracted increasing attention as a technique to fabricate inorganic whiskers, particles, and nanowires due to its low cost and large-scale production capability.22–25 This method uses a low melting salt flux as the reaction medium and inorganic salts as the reaction sources. Furthermore, in most cases, there is no need to use toxic, expensive, and unstable precursors such as organometallic compounds. After the synthesis, the remaining salts can be easily separated from the product by washing with water and recovered by recrystallization for re-use. Thus, MSS is intrinsically an economical and environmentally green synthetic technique for inorganic nanostructures.22 In this work, we report a simple MSS method to produce mullite nanowires in large quantity without the use of surfactants or templates. Aluminum sulfate (Al2(SO4)3) and silica (SiO2) act as the starting reagents and sodium sulfate (Na2SO4) serves as the molten medium. It is mixed well by ball-milling and
then heated up to 1000 °C for 3 hrs in air. Afterwards, the remaining salts are removed by washing with water, and finally, pure mullite nanowires were obtained. The morphology and microstructures of the synthesized mullite nanowires are characterized and the growth mechanism is discussed. It should be mentioned that in our preparation, about 50 grams of the mullite nanowires can be fabricated at one time, and the conversion rate is close to 100% as calculated from the raw materials. In principle, the yield of the mullite nanowires by our MSS method depends on the volume of the reaction kettle. This MSS method can be readily extended or produce other multicomponent oxide nanostructures in large amounts. The potential technological importance of the products, simplicity of the preparation procedures, and cheap precursors make this study scientifically and technologically interesting.

2. EXPERIMENTAL DETAILS

The starting materials were aluminum sulfate hydrate (Al₃(SO₄)₃·18H₂O) and amorphous silica (SiO₂) and the molten salt medium was sodium sulfate (Na₂SO₄). The Al₃(SO₄)₃·18H₂O was first calcined at 300 °C for 3 hrs to remove H₂O to obtain anhydrous Al₃(SO₄)₃. The SiO₂, Al₃(SO₄)₃, and Na₂SO₄ powders with the weight ratio of 1:8.55:16.6 were mixed by ball-milling for 30 min. The mixed powders were put into a covered alumina crucible inside a muffle furnace and heated at a rate of 10 °C/min to 1000 °C. The reaction proceeded for 3 hrs at this temperature and then the sample was cooled naturally to room temperature. After the reaction, the samples were washed by hot water several times to remove remaining salts and after drying at 100 °C for 2 h, white powders were produced.

The morphology, structure, and composition of the product were investigated by X-ray diffraction (XRD, Philips X' Pert Pro), field-emission scanning electron microscopy (FE-SEM, FEI-Sirion 2000), transmission electron microscopy (TEM, Philips CM20), high-resolution TEM (HR-TEM, JEM-2010F), selected-area electron diffraction (SAED), energy-dispersive X-ray spectroscopy (EDS, Oxford INCA 200), and inductively coupled plasmaatomic emission spectrometry (ICP-AES, IRIS Intrepid II XSP). The thermal and chemical behavior of the mixed powders was investigated by heating at a rate of 10 °C/min to 1200 °C in air, followed by thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses on the Netzsch thermal analysis instrument (STA-449/C).

3. RESULTS AND DISCUSSION

The inset in Figure 1(a) is the optical image of the final product and reveals large quantities of white powders. The SEM image in Figure 1(a) indicates that the white powders comprise nanowires. The lengths of the nanowires range from several hundreds of nanometers to micrometers. The XRD pattern acquired from the nanowires is depicted in Figure 1(b). All the diffraction peaks can be indexed to the orthorhombic mullite structure (JCPDS card, No. 15-0776), indicating that the nanowires consist of orthorhombic mullites. There are no Al₂O₃ and SiO₂ diffraction peaks in the XRD pattern, suggesting that SiO₂ and Al₂O₃ from the decomposition of Al₃(SO₄)₃ have been fully converted into mullite.

The TEM images further disclose the morphology and structures of the mullite nanowires. Figure 2(a) is a TEM image of the mullite nanowires. The diameters of nanowires range between 30 and 80 nm and their lengths vary from several hundred nanometers to micrometers. The ripple-like contrast in the TEM image may be due to strain resulting from the twisting or bending of the nanowires. Figure 2(b) is a representative TEM image of a single nanowire together with the SAED pattern (insert). The SAED pattern reveals that the mullite nanowire is a single crystal with an orthorhombic structure growing along the [001] direction. Figure 3(a) is the HRTEM image of a mullite nanowire, further suggesting that the mullite nanowire is a single crystal and almost defect free structurally. The inset in Figure 1(a) is the optical image of the final product and reveals large quantities of white powders. The SEM image in Figure 1(a) indicates that the white powders comprise nanowires.
The spacings between the lattice planes perpendicular to and parallel to the growth direction of the nanowire are 0.29 and 0.54 nm, respectively, which correspond to the \(d\)-spacings of the (001) and (110) planes of orthorhombic mullites. The results suggest that the nanowires grow along the [001] direction corroborating the SAED results. The corresponding EDS spectrum (Fig. 3(b)) shows that the nanowire is composed of Al, Si, and O. The C and Cu in EDX peaks can be attributed to the carbon-coated copper TEM grid.

Figure 4 displays the TG-DSC curve of the starting mixture heated at a rate of 10 °C/min to 1200 °C in air. The weight ratio of Na\(_2\)SO\(_4\) and Al\(_2\)(SO\(_4\))\(_3\) in the starting materials is 66:34. The binary phase diagram of Na\(_2\)SO\(_4\)-Al\(_2\)(SO\(_4\))\(_3\) suggests that Na\(_2\)SO\(_4\) (66 wt%) and Al\(_2\)(SO\(_4\))\(_3\) (34 wt%) can form low melting point Na\(_3\)Al(SO\(_4\))\(_3\) at 640 °C.\(^{27}\) Thus, the sharp endothermic peak centered at 640 °C is believed to stem from the formation of low melting point Na\(_3\)Al(SO\(_4\))\(_3\). The weight loss at 900–1050 °C is attributed to the removal of remaining water from Al\(_2\)(SO\(_4\))\(_3\) and the latter arises from the evaporation of liquid Na\(_3\)Al(SO\(_4\))\(_3\). The above analysis and characterization results indicate that single crystal mullite nanowires have been produced in large quantities. Since no catalyst, gaseous precursors, template, and surfactants are used, common mechanisms for nanowires such as vapor–liquid–solid growth,\(^{28}\) vapor–solid growth\(^{29}\) and template confined growth\(^{30}\) cannot be employed to explain the formation process of these mullite nanowires. In our experiment, if we directly mix Al\(_2\)O\(_3\), SiO\(_2\), and Na\(_2\)SO\(_4\) with the same molar ratio and heat the mixture to 1000 °C for 3 h, mullite nanowires cannot be synthesized. This indicates that Al\(_2\)(SO\(_4\))\(_3\) is necessary.
On the other hand, if Na₂SO₄ is not used in the experiment, mullite nanowires cannot be produced. During the heating process above 640 °C, solid Na₂SO₄ (66 wt%) and Al₂(SO₄)₃ (34 wt%) first react to form low melting point liquid Na₂Al(SO₄)₃ by Reaction (1). Above 900 °C, liquid Al₂(SO₄)₃ begins to decompose into Al₂O₃ and SO₃(g) by the Reaction (2). The formed Al₂O₃ or Na₃Al(SO₄)₃ can react with slightly soluble SiO₂ in liquid Na₂SO₄ to produce 3Al₂O₃·2SiO₂ and gaseous SO₃ via Reactions (3) and (4). As more mullites are formed, the supersaturated mullite species precipitate in the liquid Na₂SO₄ medium due to low solubility and these precipitates serve as nucleation sites for the epitaxial growth of the mullite nanowires according to Reactions (3) and (4).

$$3\text{Na}_2\text{SO}_4(l) + \text{Al}_2\text{(SO}_4)_3(g) = 2\text{Na}_2\text{Al(SO}_4)_3(l)$$  \hspace{1cm} (1)

$$\text{Al}_2\text{(SO}_4)_3(l) \rightarrow \text{Al}_2\text{O}_3(l) + 3\text{SO}_3(g)$$  \hspace{1cm} (2)

$$3\text{Al}_2\text{O}_3(l) + 2\text{SiO}_2(l) = 3\text{Al}_2\text{O}_3(l) + 2\text{SiO}_2(g)$$  \hspace{1cm} (3)

$$2\text{Na}_2\text{Al(SO}_4)_3(l) + 2\text{SiO}_2(l) + \text{Al}_2\text{(SO}_4)_3(l)$$
$$= 3\text{Al}_2\text{O}_3(l) + 2\text{SiO}_2(g) + 3\text{Na}_2\text{SO}_4(l) + 9\text{SO}_3(g)$$  \hspace{1cm} (4)

The overall chemical reaction is:

$$3\text{Al}_2\text{(SO}_4)_3(l) + 2\text{SiO}_2(l) = 3\text{Al}_2\text{O}_3(l) + 2\text{SiO}_2(g) + 9\text{SO}_3(g)$$  \hspace{1cm} (5)

After the Al₂O₃·2SiO₂ nanowires are formed, the remaining Na₂SO₄ can be easily separated from the product by rinsing with water and recrystallized later for re-use. ICP-AES analyses reveal that the Na content in the product is only 0.14 wt%. Hence, pure mullite nanowires can be synthesized by the MSS method. In this growth process, the liquid Na₂SO₄ flux serves three functions. Firstly, Na₂SO₄ and Al₂(SO₄)₃ form low melting point Na₂Al(SO₄)₃. Secondly, SiO₂(l) and in situ generated Al₂O₃(l) are slightly soluble in liquid Na₂SO₄ and atomic-scale mixing of the reactants in the liquid medium can be achieved. Along with the fast diffusion of the species in the liquid medium, the reaction can be completed at a relatively low temperature and/or in a short time. Thirdly, the molten Na₂SO₄ between the nanowires could prevent the conglomeration of mullite enabling formation of the mullite nanostructure.

4. CONCLUSION

Single-crystal mullite nanowires have been synthesized in large quantities by a molten salt method. The starting materials, Al₂(SO₄)₃, and SiO₂, react in a molten Na₂SO₄ medium at 1000 °C for 3 hrs producing mullite nanowires without the use of surfactants or templates. After the synthesis, the remaining salts can be easily separated from the products by rinsing with water. The process is economical and environmentally green, boiling well for large-scale production. The diameters of the mullite nanowires are 30–80 nm and their lengths vary from several hundreds of nanometers to micrometers. The growth mechanism is discussed. This method is can be extended to produce other oxide nanostructures in large quantities.

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References and Notes

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