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Effect of the addition of glucose on the fabrication of nanosized mullite from a sol–gel by spark plasma sintering

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Abstract

Nanosized mullite with an average crystal size below 100 nm was synthesized by spark plasma sintering combined with a sol–gel process and the addition of glucose to the precursor materials. A suppression of grain growth was achieved by adding glucose. The influence of glucose was studied by evaluating samples with a glucose/Al^{3+} ratio of 0:1, 1:1, and 3:1, respectively. The sample prepared without glucose was the least homogeneous and showed a low relative density and irregular microstructure after sintering. In contrast, the sample prepared with a glucose/Al^{3+} ratio of 3:1 was the most homogeneous, leading nearly full densified mullite with nanosized grains at lower sintering temperature.

Keywords: Mullite; Glucose; Sol–gel; Nanomaterial; Spark plasma sintering

1. Introduction

Due to its low thermal expansion coefficient, low thermal conductivity, high thermal stability, high creep resistance and good stability in harsh chemical environments, mullite is a widely used ceramic material for structural applications.[1–5] Although it offers many advantages, the brittle nature of mullite limits the fabrication of advanced materials and restricts its application potential. Novel ceramic materials with nanometer-sized grains provide a possibility to overcome these challenges.[6,7] The fabrication of dense bulk nanosized oxides is very challenging since grain growth inevitably occurs at the relatively high sintering temperatures that are necessary for the densification of the materials. Finding a feasible synthesis route for nanosized mullite is therefore highly desirable.

In order to obtain dense nanoceramic materials, two important factors must be considered: firstly, a nanocrystalline powder with good chemical homogeneity as well as a high chemical purity is required. Secondly, the sintering technology has a significant influence on the preparation of nanometer-scale mullite ceramic materials.

The sol–gel process is an effective method to synthesize mullite precursors of high purity and homogeneity.[8] The mullite crystallization mechanism depends on the chemical homogeneity of the silicon and aluminum precursors.[9] Chemically synthesized precursors typically converted into mullite at temperatures in the range from 850 to 1350 °C. If the precursor exhibits a high degree of homogeneity, mullite crystallization can be achieved at comparatively low temperatures.[10] However, the homogeneity of the precursors depends on the hydrolysis and condensation rate of the sol–gel process. Controlling the hydrolysis and condensation rates of the starting materials is very important in order to increase the precursor homogeneity.[11,12] Otherwise, phase segregation might occur, which not only promotes the crystallization of undesirable phases, such as α-alumina and spinel, but also results in a high mullite crystallization temperature. In addition, the homogeneity level also can be controlled with the help of chemical additives, such as carboxylic acids or functional alcohols, which act as chelating agents and modify the precursor reactivity.[13,14]

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Some studies reported on the use of organic polydentate ligands, like ethylene glycol, during mullite synthesis via the sol–gel process because these organic ligands are expected to be able to control the polymerization step of the starting materials by acting as a bridge between aluminum and silicon atoms, since the ethoxy group of tetraethyl orthosilicate molecules can easily be replaced by the hydroxyl groups of these ligands.[15,16] Furthermore, the addition of glucose to precursor materials has been applied in different roles in the synthesis of materials. Shang et al.[17] demonstrated the use of glucose as a fuel that decreased the crystallization temperature for the synthesis of nanocrystalline $BaFe_{12}O_{19}$ powders. Recently, alumina nanoparticles were synthesized in the presence of glucose which increased the homogeneity of precursor by Naskar[18] So far, there is rare report focused on the influence of glucose on the synthesis for mullite powders.

The sintering of stoichiometric pure mullite requires pressure-assisted sintering methods, like hot-pressing and hot-isostatic pressing, to achieve a high degree of densification. As an alternative, spark plasma sintering (SPS) is an efficient sintering method that allows for the rapid consolidation of mullite ceramics at comparatively low temperatures. Zhang et al.[19] fabricated dense mullite ceramics from monophasic precursors by SPS at 1450 °C with a heating rate of 100 °C min^{-1} under pressure of 30 MPa. The grain size, however, was larger than 300 nm.

In this paper, we present a novel method to fabricate nanosized mullite by combining a sol–gel method with the addition of glucose and SPS. The effects of glucose on the synthesis of mullite nanoparticles via the sol–gel method were studied in detail. Furthermore, we present a low-temperature sintering method to obtain nanosized mullite ceramics with a high relative density from nanocrystalline powders with added glucose.

2. Experimental details

2.1. Sample preparation

Gels with the stoichiometric composition of mullite, i.e. an Al:Si ratio of 3:1, were prepared from aluminum nitrate nonahydrate (ANN) and tetraethoxysilane (TEOS). Glucose was added using glucose/Al^{3+} molar ratios of 0, 1 and 3, with the resulting samples denoted as G0, G1, G3, respectively. The procedure for synthesizing the gels can be briefly summarized as follows: The stoichiometric amount of TEOS was dissolved in absolute ethanol and water and stirred at 30 °C for 24 h prior to the prehydrolysis. ANN and glucose were then individually dissolved in water, stirred at 60 °C for 2 h and then mixed together. Next, the TEOS solution was added to the mixture, which was stirred under reflux at 60 °C for 24 h. After refluxing, the resulting mixture was poured into a beaker, covered with filter paper and aged for 6 days until the mixing solution became viscous. The resulting gel was dried at 110 °C for 2 days and then ground into powders. The gel powders were finally calcined at 800 °C for 10 h at an annealing rate of 2 °C min^{-1} in order to remove water and organic residues.

The mullite precursor powders were thermally treated at different temperatures, i.e. 900 °C, 1000 °C, 1100 °C, and 1150 °C. Then, 3 g of the thermally treated powders were poured into a graphite mold with an inner diameter of 20 mm and an outer diameter of 40 mm, and sintered in vacuum at a temperature in the range from 1250 °C to 1400 °C for 10 min by SPS at a heating rate of 100 °C min^{-1}. The temperatures were measured with an optical pyrometer focused on the surface of the graphite die and automatically regulated from 600 °C to the final sintering temperature. A pressure of 80 MPa was applied to the samples from the beginning and then held constant until the end of the sintering process. The thickness of the sintered specimens was about 2 mm.

2.2. Sample characterization

The crystal structure and degree of crystallinity of the mullite samples was studied by X-ray diffraction (XRD) analysis with the patterns recorded on an X-ray diffractometer (D/MAX-RB, Rigaku, Japan) operated at 40 kV and 40 mA using CuKα radiation, a scan step of 0.02° and a scan rate of 4° min^{-1} within the 2θ range from 10° to 90°. Fourier transform infrared spectra (FT-IR) were recorded on a Nicolet 6700 FTIR spectrometer. The field emission scanning electron microscopy (FESEM, Hitachi S-4800) and high-resolution transmission electron microscope (HRTEM, JEM-2010F) were used to observe the structure and morphology of sample. The densities of the sintered specimens were determined by applying the Archimedes method. The relative bulk densities were calculated based on the theoretical density of mullite (3.17 g cm^{-3}).

3. Results and discussion

3.1. Synthesis of the mullite nanocrystalline powders

Fig. 1 illustrates the crystallization process of the samples G0, G1, G3 at different annealing temperatures. At a temperature of 900 °C, both the sample G1 and the sample G3 show a small amount of tetragonal mullite denoted as t-mullite together with an Al–Si spinel phase. For sample G0, α-alumina and the Al–Si spinel were found, but no mullite crystals. Spinel is another phase that can appear during the aluminosilicate synthesis and exhibits a low degree of crystallinity and XRD peaks at 46° and 67°.[20–22] The formation of the α-alumina phase during the mullite synthesis is considered to be an indicator of precursor heterogeneity.[23]

When the samples were annealed at 1000 °C, the XRD profile of sample G0 did not show a change in crystal composition, i.e. both the spinel and α-alumina phase were still observed. However, the splitting of the peaks around 26° suggests that an orthorhombic mullite phase designated as o-mullite crystallized in sample G3. The main difference between the samples with different amounts of glucose is the formation of o-mullite in the samples G1 and G3.

As the temperature was further increased to 1100 °C, t-mullite appeared in sample G0 as well as α-alumina and spinel, while the crystalline composition of G1 did not change. In sample G3, o-mullite was the only remaining crystalline phase; there