Research Article

Direct Preparation of Y_2SiO_5 Nanocrystallites by a Microwave Hydrothermal Process

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A novel fabrication technique of yttrium silicate (Y_2SiO_5) nanocrystallites has been investigated by a microwave hydrothermal process with a later heat treatment. The prepared powders were analyzed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermal analysis, and field emission scanning electron microscopy (FESEM). Results show that high-purity yttrium silicate (Y_2SiO_5) powders can be synthesized by the microwave hydrothermal process with a later heat treatment at 700°C for 2 h. The Y_2SiO_5 precursor powders prepared by microwave hydrothermal process without heat treatment are weak crystallization, which shows an irregular and cotton-fiber-like morphology. After the heat treatment at 700°C for 2 h, well crystallized phase-pure Y_2SiO_5 powders with 400–600 nm grainy morphology are achieved. Further heat treatment at higher temperature will result in the sintering and serious agglomeration of the powders. The formation process of Y_2SiO_5 nanocrystallites was explained based on the photographs of SEM.

1. Introduction

Yttrium silicate (Y_2SiO_5) is a well-known important luminescent host material for various rare-earth activators. $\text{Y}_2\text{SiO}_5:\text{Tb}^{3+}$ is one of the best green emitting cathodoluminescent phosphors [1, 2]. $\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$ was found to be a promising candidate for coherent time-domain optical memory (CTDOM) applications [3]. Due to its high melting point, low evaporation rate, equivalent thermal expansion coefficient, and low oxygen permeation constant [4], yttrium silicates is considered as one of the best antioxidation coating for C/C composites [5–7]. But the preparation technology has great influence on the morphologies and properties of Y_2SiO_5 [8]. Recently, some methods for the preparation of Y_2SiO_5 nanocrystallites have been reported, such as solid-state reaction [9], hydrothermal method [10], and sol-gel technique [11]. However, during the above-mentioned reactions process, high reaction temperature, long heating time, or high-intensity milling process are required. It is difficult to guarantee high-purity yttrium silicate crystallites due to their complex crystal structures. In comparison with

the traditional method, the microwave hydrothermal process has been proved to be an economic and effective way to prepare inorganic nanocrystallites [12]. The major merit of the microwave hydrothermal process is a rapid heating to temperature and fast kinetics of crystallization, which are able to save energy and time for preparing the materials and useful to synthesize pure nanocrystallites.

In the present work, in order to synthesize high-purity yttrium silicate (Y_2SiO_5) crystallites, a microwave hydrothermal process with a later heat treatment has been adopted. The influences of processing factors on the phase and morphologies of the Y_2SiO_5 crystallites were particularly investigated.

2. Experimental

2.1. Synthesis of Y_2SiO_5 Nanocrystallites. Analytical $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ and NaOH were selected as main source materials. Firstly, 12 mL 0.5 mol·L⁻¹ $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ aqueous solution, 6 mL 0.5 mol·L⁻¹ $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ aqueous solution, 24 mL 0.5 mol·L⁻¹ NaOH

- (1) Thermocouple (4) Solution
 (2) Pressure sensor (5) PTFE/TFM reaction vessel
 (3) PTFE/TFM cover (6) High temperature shield

FIGURE 1: Schematic figure of the microwave-hydrothermal apparatus. (1) thermocouple, (2) pressure sensor, (3) PTFE/TFM cover, (4) solution, (5) PTFE/TFM reaction vessel, and (6) high-temperature shield.

FIGURE 2: XRD patterns of the powders prepared by microwave hydrothermal process (a) without heat treatment and (b) with heat treatment at 700°C for 2 h.

aqueous solution were added into 100 mL glass beaker. After being agitated for 30 minutes, the above solution was poured into 70 mL hydrothermal autoclave. Secondly, the autoclave was sealed and put into a microwave digestion system as shown in 1. During the reaction process, the autoclave temperature was kept at 200°C. After 20 minutes, the autoclave was taken out from the microwave-hydrothermal apparatus and cooled naturally at room temperature. Then, the precipitates were filtered, washed by deionized water and isopropyl

FIGURE 3: FTIR spectra of the powders prepared by microwave hydrothermal process (a) without heat treatment and (b) with heat treatment at 700°C for 2 h.

alcohol and later dried at 80°C for 1 h. Finally, the microwave hydrothermal resulted Y_2SiO_5 precursor powders were heat treated at 700°C and 900°C for 2 h, respectively. The pure Y_2SiO_5 nanocrystallites were achieved.

2.2. Characterization Techniques. The as-prepared powders were characterized by D/max 2200 PC X-ray diffraction (XRD), Model 2000 fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TG), JSM-6700 field emission scanning electron microscopy (FESEM), and JEM-3010 transmission electron microscopy (TEM).

3. Results and Discussion

3.1. XRD Analysis. Figure 2 shows the XRD patterns of the powders prepared by microwave hydrothermal process. Figure 2(a) is the powders without heat treatment, and Figure 2(b) is the powders with heat treated at 700°C for 2 h. The patterns are all analyzed by JCPDS (Joint of committee on powder diffraction standards) data base. Only the amorphous structure is observed in the Y_2SiO_5 powders without heat treatment as illustrated in Figure 2(a). During the microwave hydrothermal process, no homogeneous nucleation and temperature gradient condition will be achieved. But the reaction solution will be cooled down quickly after the microwave hydrothermal reaction is finished, which may result in the weak crystallization of the precursor powders. But the strong peak intensity of Y_2SiO_5 is observed as shown in Figure 2(b), which infers that heat treatment is better for high purity of the synthesized crystallites.

3.2. FTIR Analysis. Figure 3 shows the FTIR spectra of the as-prepared powders. Figure 3(a) shows the presence of a broad band at 2700–3600 cm^{-1} , which can be attributed to

FIGURE 4: TG (a) and DSC (b) curves obtained from Y_2SiO_5 precursor.

FIGURE 5: FESEM images of the precursor powders prepared by microwave hydrothermal process (a) without heat treatment, (b) with heat treatment at 700°C for 2 h and (c) with heat treatment at 900°C for 2 h.

the C–H and O–H stretching frequencies of the surface-absorbed isopropanol molecule and alkoxy groups. The peak at 1651 cm^{-1} is due to the presence of O–H stretching frequencies, which comes from water. Additionally, the features in the vicinity of 1385 cm^{-1} and 1519 cm^{-1} are assigned to $-\text{CH}_3$ and C–O bonds stretches arising from alkoxy groups. The other bands at 991 cm^{-1} and 671 cm^{-1} are the characteristics of Si–O group. Any bands associated with Y–O are at the band numbers of 400 cm^{-1} and are outside of the measured range.

For the crystallites obtained after heat treatment at 700°C for 2 h as shown in Figure 3(b), only the vibration bands relative to Si–O bonds and $-\text{CH}_3$ bonds were detected, which infers that the volatilization of water and decomposition of organo group happened during the later heat treatment.

3.3. DSC and TG Analysis. Figure 4 shows the TG (a) and DSC (b) curves obtained from the prepared Y_2SiO_5 precursor. Figure 4(a) displays two main weight losses at the temperature range of 30°C–456.9°C (about 45 wt%) and 456.9°C–1000°C (about 5 wt%). Based on the FTIR analysis, the first weight losses at 30°C–456.9°C is due to the evaporation of weakly bonded water (83.8°C) and the group that absorbed on the surface of the yttrium silicate

precursor (83.8°C–451.5°C), which result in the generation of an endothermic peak (83.8°C) and an exothermic peak (456.9°C) as shown in Figure 4(b). There exists another two exothermic peaks shown in Figure 4(b). One is at 738.6°C, and the other is near 1130.3°C. The exothermic peak appeared at 738.6°C may result from the crystallization of the Y_2SiO_5 precursors, which can be demonstrated by the XRD analysis shown in Figure 2(b). The other exothermic peak generated at 1130.3°C may be due to the phase transition of yttrium silicate crystallites according to Boyer and Derby research [11].

3.4. FESEM Analysis. Figure 5 shows the FESEM images of the precursor powders prepared by microwave hydrothermal process. Figure 5(a) indicates that the irregular particles with cotton-fiber-like morphology are obtained from the microwave hydrothermal process. After heat treatment at 700°C for 2 h, 400–600 nm grainy morphology is observed (Figure 5(b)), which is due to the crystallization of Y_2SiO_5 precursor at high temperature according to the analysis from Figures 2 and 4. However, after the heat treatment at 900°C for 2 h, serious agglomeration of the powders is obtained. These indicate that higher heat treatment temperature will result in the crystallization and further sintering, which

FIGURE 6: Schematic representation of the microwave hydrothermal synthesis of Y_2SiO_5 crystallites from solution.

infers that the heat treatment condition should be taken into more consideration in order to obtain an optimal crystal structure.

3.5. Formation Process of Crystallites. According to Aparicio and Durán [4], the formation of Y_2SiO_5 crystallites under solution condition is based on the reaction shown in (1)–(3). During the microwave hydrothermal process illustrated in Figure 6, $Y_2(SiO_3)_3$ and $Y(OH)_3$ will be generated in the early period in the reaction. According to Wang et al. [13] Fang et al. [14], and Leskelä and Jyrkäs [15], the formation of Y_2SiO_5 crystallites is considered as a three-step process from the observation of the SEM. (a) The formation of nanoclusters: $Y_2(SiO_3)_3$ and $Y(OH)_3$ will act as nanoseeds, which will result in the formation of nanofibers or nanowires Y_2SiO_5 precursor under microwave hydrothermal condition. (b) Aggregation: a large number of nanoclusters cluster together, and nanofibers are formed. (c) Growth: the growth of the nanofibers. During the microwave hydrothermal process, large numbers of hydrogen will be absorbed on surface of the nanowires or nanofibers due to its high surface energy, which will result in the formation of cotton-fiber-like morphology of the Y_2SiO_5 precursor. Finally, after the later heat treatment at $700^\circ C$ for 2 h, a crystallization process has occurred and 400–600 nm grainy morphology is formed

Based upon the experimental results, the microwave hydrothermal process as an ecofriendly method could be applied to the preparation of Y_2SiO_5 nanocrystallites although there exists some ambiguities to be clarified in future work.

4. Conclusions

High-purity yttrium silicate (Y_2SiO_5) crystallites can be synthesized by the microwave hydrothermal process with a later heat treatment. The Y_2SiO_5 precursor powders prepared by microwave hydrothermal process are weakly crystallized, which show cotton-fiber-like morphology. Large amount of water and organic group can be detected in the precursor, the volatilization of water and decomposition of organic group happened at the temperature range of $30^\circ C$ – $451.5^\circ C$, and the crystallization of the Y_2SiO_5 precursors and decomposition of remnant organic group are taken place at the temperature range of $451.5^\circ C$ – $1000^\circ C$. After the heat treatment at $700^\circ C$ for 2 h, well-crystallized phase-pure Y_2SiO_5 powders with 400–600 nm grainy morphology are achieved. Further heat treatment at higher temperature will result in the sintering and serious agglomeration of the powders.

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