Morphology-controlled synthesis of yttrium hafnate by oxalate co-precipitation method and the growth mechanism

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\textbf{A B S T R A C T}

Yttrium hafnate (Y\textsubscript{2}Hf\textsubscript{2}O\textsubscript{7}) precursor was prepared by mixing yttrium nitrate and hafnium (IV) chloride with ammonium oxalate aqueous solution. Yttrium hafnate powders with different morphologies were obtained by decomposition of the precipitate precursor at 800 °C for 4 h. The as-prepared particles were characterized by thermo gravimetric analysis (TGA), X-ray diffraction analysis (XRD) and field-emission scanning electron microscopy (FE-SEM). The concentration of the surfactant polyethylene glycol 6000 (PEG6000) was found to play a key role on the morphology of the particles. The possible mechanism of the morphology variation was proposed.

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1. Introduction

The pyrochlore-type compounds A\textsubscript{2}B\textsubscript{2}O\textsubscript{7} (A is +3 valence, B is +4 valence) are widely researched for their unique structures and potential applications. This structure exhibits space group \textit{Fm\textsubscript{3}m} (225) and can be considered as an ordered defective fluorite [1]. This type compounds have been researched for solid-oxide fuel cells [2], dielectric materials [3–5], thermal barrier coatings [6,7], catalysts [8], and immobilization of actinides in nuclear waste [9,10]. In the nuclear field, a recent interest is their potential applications as materials for transmutation of the so-called minor actinides, americium and curium [11].

Different kinds of synthesis methods for the pyrochlore-type compounds have been developed. The rare-earth-metal zirconates (RE\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}) have been synthesized by many methods, including low-temperature solid reaction, co-precipitation, sol–gel, hydrothermal and hydrazine methods [12–17]. To the best of our knowledge, few reports about the preparation of Y\textsubscript{2}Hf\textsubscript{2}O\textsubscript{7} powders have been found except that Liao et al. [18] prepared Y\textsubscript{2}Hf\textsubscript{2}O\textsubscript{7} nano-powders by combustion method. Y\textsubscript{2}Hf\textsubscript{2}O\textsubscript{7} is a promising candidate for scintillator, which has potential application in high-energy nuclear medical fields such as computer tomography (CT) and positron emission tomography (PET). However, morphology-controlled Y\textsubscript{2}Hf\textsubscript{2}O\textsubscript{7} powders have not been investigated. As known to all, morphology-controlled synthesis is a goal of modern materi-

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Fig1.png}
\caption{The XRD pattern of the powders calcined at 800 °C for 4 h (insert: TGA curve of the precursor).}
\end{figure}
Table 1
Sample tags under different experimental conditions.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>PEG6000 (%)</th>
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<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>25</td>
<td>X1</td>
</tr>
<tr>
<td>50</td>
<td>Y1</td>
</tr>
<tr>
<td>80</td>
<td>Z1</td>
</tr>
</tbody>
</table>

als because of the importance of the shape and texture of materials in determining their widely varying properties [19–23]. Many morphology-controlled synthetic methods have been reported, including controlled precipitation [24], seeded growth [25], and confined synthesis in structured templates [26,27]. Particularly, synthetic polymers and surfactants were found to drastically change the morphology of ceramic particles [28].

In this paper, we report the synthesis of Y$_2$Hf$_2$O$_7$ powders by oxalate co-precipitation method and use the surfactant PEG6000 to modify the morphologies. The influence of reaction temperature and concentration of surfactant on the morphologies of the

Fig. 2. SEM images of Z1, Z3, Z5 and Z6 prepared at 80 °C with different concentrations of surfactant: (a) 0%; (b) 0.6%; (c) 1.2%; (d) 1.5%; correspondingly, A, B, C and D are Y$_2$Hf$_2$O$_7$ precursors and a, b, c and d are the powders calcined at 800 °C for 2 h, respectively.
2. Experimental procedure

The starting materials were yttrium nitrate (Y(NO₃)₃, 99.9%), hafnium (IV) chloride (HfCl₄, 99.0%), diammonium oxalate monohydrate ((NH₄)₂C₂O₄·H₂O, 99.5%), ammonia (NH₃·H₂O ∼ 25%) and polyethylene glycol 6000 (PEG6000). As denoted in Table 1, different concentrations of surfactant PEG6000 (wt%: 0, 0.3%, 0.6%, 0.9%, 1.2% and 1.5%) and several reaction temperatures (involved 25 °C, 50 °C and 80 °C) were investigated.

In a typical procedure, 80 mL salt solution of Y(NO₃)₃ and HfOCl₂ (hydrolyzed from HfCl₄) was prepared by dissolving the corresponding salts into de-ionized water. The concentration of total cations was 0.125 mol/L with the molar ratio of Y:Hf equal to 1:1. An appropriate concentration PEG6000 was used as surfactant. 50 mL (NH₄)₂C₂O₄ aqueous solution with a concentration of 0.3 mol/L was used as the precipitate solution. The precursor precipitate was produced by dropping (NH₄)₂C₂O₄ into the salt solution under ultrasonic agitation in a water bath with an appropriate temperature for 30 min. The experiment was conducted at pH 7, which was adjusted by the addition of appropriate amounts of ammonia. Then the reaction solution was aged at room temperature for 6 h. The precipitate was separated by filtration and washed repeatedly with de-ionized water to remove chloride and nitrate ions. After dried at 100 °C for 12 h in a vacuum drying chamber, the precipitate was calcined at 800 °C for 4 h in a muffle furnace, with a heating rate of 5 °C/min.

The precipitate precursor was characterized by thermo gravimetric analysis (TGA) (Netzsch STA-449c, Germany) under air flow at a heating rate of 10 °C/min. X-ray powder diffraction was performed on a Japan Rigaku K/max-γAX-ray diffractometer (Model D/MAX-2550 V, Rigaku Industrial Corporation, Japan) with Cu Kα radiation (1.54178 Angstrom). The morphologies of the powders were observed by field-emission scanning electron microscopy (JSM-6700F, JEOL, Japan).

3. Results and discussion

Fig. 1 shows the XRD pattern of the powders calcined at 800 °C for 4 h and the TGA curve of the precursor from room temperature to 1000 °C. According to the inserted TGA curve in Fig. 1, it can be seen that all the weight loss happened below 720 °C, which indicated that the decomposition of precursors and the formation of Y₂Hf₂O₇ were completed till this temperature. Also, the precursor calcined at 800 °C for 4 h resulted in the pure crystalline Y₂Hf₂O₇, which is in agreement with the TGA results. The crystal phase of the powders can be identified with cubic system (space group: Fm₃m (225)) by XRD results. The sharp diffraction peaks suggested the well developed Y₂Hf₂O₇ crystals.

Fig. 2 is the SEM images of Y₂Hf₂O₇ precursor prepared at 80 °C and the corresponding powders calcined at 800 °C for 2 h with the different concentrations of surfactant from 0, 0.6, 1.2, to 1.5 wt.%. A strong relationship was observed between the precursor powders and the calcined powders. Platelets, rod-like or spherical shape for a given precursor (Fig. 2A, B, C, and D) actually led to the similar shapes for the corresponding Y₂Hf₂O₇ powders (Fig. 2a, b, c and d). With the increasing concentration of PEG6000, the mor-

Fig. 4. SEM images of X6, Y6 and Z6 precursors prepared at different temperatures: (a) 25 °C; (b) 50 °C; (c) 80 °C, respectively.
shown that polycrystalline can break apart, depending on normal inorganic minerals, PEG chains can be adsorbed on the surface of precursor particles. Here the possible mechanism of the morphology formation was proposed as shown in Fig. 3. If there is no PEG6000, the precursor particles agglomerate in platelet-like shape (Fig. 3I) and are inhomogeneous. Addition of PEG6000 leads to the homogeneous and small-sized rod-like shape (Fig. 3II and III). This is because surfactant PEG can affect the nucleation and growth of particles, which consequently can modify particle morphology and size. According to the thermodynamic theory, minimization of free energy of a polycrystalline granular system corresponds to a balance between variations of surface energy (in the air: \( E_{\text{surf}} = y_{\text{sg}} A_{\text{sg}} \)) where \( y_{\text{sg}} \) is the solid-gas surface tension and \( A_{\text{sg}} \) is the solid-gas surface area; in solution, analogically: \( E_{\text{surf}} = y_{\text{ss}} A_{\text{ss}} \) and variations of interface energy (\( E_{\text{interf}} = y_{\text{ss}} A_{\text{ss}} \)) which reduced the growth rate in solution and helped the particles break up in the air (Fig. 3II). Consequently, the very accumulative clusters were not inclined to exist and then the homogenous rod-like particles with small diameter were obtained. If the concentration increased furthermore, these rods-like clusters seemed to break up into dissipative particles-chains (PEG chains adsorbed on the surface of precursor particles). These particles-chains were easy to change into spherical agglomerations (Fig. 3IV). After being calcined, the PEG6000 decomposed and then the spherical shells yielded.

Fig. 4 shows the SEM images of the Y2Hf2O7 powders prepared at different reaction temperatures ((a) X6, 25 °C; (b) Y6, 50 °C; (c) Z6, 80 °C) with 1.5 wt.% PEG6000. All the particles exhibited spherical shape. However, agglomeration occurred and decreased along with the increase of the reaction temperature. The particle size of X6, Y6 and Z6 was \( \sim 150\) nm, \( \sim 150\) nm and \( \sim 250\) nm, respectively, which indicated that a higher reaction temperature resulted in a larger particle size. The reaction temperature had an impact on the activity of the surfactant and the growth rate of the precursors. The PEG molecules may be more active and homogenous at a higher reaction temperature, which leads to the better dispersion of precursors. The growth rate of particles is rapid at higher temperature and therefore the bigger particles resulted.

4. Conclusion

Pure pyrochlore structure \( \text{Y}_2\text{Hf}_2\text{O}_7 \) has been prepared by oxalate co-precipitation method. The morphology of the powders after heat treatment was found similar to the corresponding precursor. Platelet, rod, and spherical shape \( \text{Y}_2\text{Hf}_2\text{O}_7 \) powders were obtained by controlling the concentration of the surfactant PEG6000. The reaction temperature mainly affects the particle size of the powders. The possible growth mechanism for these variations in morphology was proposed.

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References


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